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Preliminary Report on the International Energy Agency Mode of Occurrence Inter-laboratory Comparison: Phase I; USGS Results

by

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Introduction

Understanding the mode of occurrence of trace-elements in coal is an important part of predicting element behavior and determining element mobility during coal utilization and storage. A wide range of techniques is currently used to make these determinations. To generate information on modes of occurrence some labortories rely on analysis of density separates, others use various solvents to selectively leach inorganic constituents and yet others use microbeam instruments such as scanning electron microscopes and electron microprobes. No two laboratories use the same approach or rely on the same assumptions. Under these circumstances is it possible to confidently compare the results of different laboratories? To answer this question, the U.S. Geological Survey (USGS) and eight other laboratories* are participating in an international laboratory comparison study of homogenized coal samples. The International Energy agency (IEA) has endorsed this inter-laboratory study and has agreed to publish a summary comparing the results. To date, samples of four coals have been distributed to participating laboratories. Mode of occurrence (chemical speciation) determinations for three of these coals, Gascoigne-Wood #2 (England), Illinois #6 (USA), and Wyee (Australia), are presented in this paper. Results from the 4th coal from Canada will be presented when the data are completed. Information on the rank, ash content and sulfur content of these three samples is given below (Table 1). USGS bulk chemical data and preliminary bulk data from six other participating labs are given in Appendix 1. Because these data are preliminary only the USGS results are identified. We have just begun work on the fourth coal and results are not yet available.

As part of this study each of the participating laboratories* are determining trace element modes of occurrence using their own respective techniques. All procedures are unique. Three labs are using leaching procedures, three labs are using density procedures and several labs are using SEM and/or microprobe as their primary or secondary method of determining modes of occurrence. The USGS modes of occurrence data are presented here with comparisons to other results in specific cases. The complete mode of occurrence data set and possibly a statistical comparison of the bulk chemical results will be given a final report published by the IEA.

For bulk analysis, a combination of methods is used, including inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), instrumental neutron activation analysis (INAA), and element specific techniques such as cold vapor atomic absorption (CVAA) for Hg

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* The University of Kentucky; U.S. Geological Survey; Energy (USGS) and Environmental Research Center, University of North Dakota (EERC); Geological Survey of Canada; Imperial College, London, England; University of Sheffield (England); University of Wales (Cardiff, Wales); Consejo Superior de Investigaciones Cientificas (CSIC; Barcelona, Spain); and the Commonwealth Scientific and Industrial Research Organization (CSIRO; Australia).

and hydride generation atomic absorption (HGAA) for Se. Element mode of occurrence determinations are based on an iterative selective leaching approach that is used in conjunction with scanning electron microscopy/energy dispersive X-ray analysis (SEM/EDX), X-ray diffraction (XRD), and electron probe microanalysis (EPMA). Other quantitative or semi-quantitative techniques used in the mode of occurrence determinations include, low temperature ashing, and analysis of sulfur forms.

Where possible, our results are compared with data from other laboratories, obtained using differing techniques. These alternate techniques include analysis of density separates to determine element affinities, and XAFS (X-ray absorption fine structure) analysis to determine the speciation of certain elements in coal. This comparison is intended to identify elements for which similar results are obtained by a variety of techniques, and those for which there are contradictory results or interpretations. In doing so, this study serves to identify areas or techniques in need of improvement.

Table 1. Characteristics of three bituminous coal samples examined in International Laboratory Comparison Study (values in weight percent)

Sample Bed **Country**	**Ash**	**Total Sulfur**
Wyee Australia	23.7	0.36
Gascoigne Wood #2 Great Britain	15.8	1.27
Illinois #6 United States	10.4	3.78

Methods

Bulk Chemistry

Forty-eight elements were analyzed in each of the three coal samples. Twenty-eight elements (Na, K, Rb, Cs, Sr, Ba, Sc, Cr, Fe, Co, Ni, Zn, As, Se, Sb, W, Hf, Ta, Th, U, La, Ce, Nd, Sm, Eu, Tb, Yb, and Lu) were determined by INAA on the whole coal using procedures similar to those of Palmer (1997). Eight major oxides (Al_2O_3, CaO, Fe_2O_3, K_2O, MgO, Na_2O, Si_2O, and TiO_2) and fifteen trace elements (Li, Be, Sr, Ba, Sc, V, Cr, Mn, Co, Ni, Cu, Zn, Th, Y and B) were determined on 550° C ash by ICP-AES using procedures similar to those of Briggs (1997). Thirteen elements (Rb, Cs, Mo, Cd, As, Sb, Tl, Pb, U, Ga, Ge, Nb) were determined on 550 °C ash by ICP-MS using techniques similar to those of Meier (1997). Mercury was determined by CVAA using techniques similar to those of O'Leary (1997). Selenium was determined by HGAA (O'Leary, 1997). For the eighteen elements which were determined by more than one technique the results with the lowest uncertainty were used. The technique used for each element are given in Appendices 1A-1C. The combination of techniques used by the USGS provides data on a large number of elements with great reliability (Palmer and Klizas, 1997).

Selective Leaching

The sequential selective leaching procedure used in this study is similar to that described by Palmer et al. (1993), modified from that of Finkelman et al. (1990). Duplicate 5 g coal samples were sequentially leached with 35 ml each of 1N ammonium acetate (CH_3COONH_4), 3N hydrochloric acid (HCl), concentrated hydrofluoric acid (HF; 48%) and 2N (1:7) nitric acid (HNO_3) in 50 ml polypropylene tubes. Each tube was shaken for 18 hrs using a motorized shaker. Because gas can form during the leaching procedure, it is necessary to enclose each tube in double polyethylene bags, which allow gas to escape, but prevent the release of liquid. After leaching, the coal slurries were centrifuged and the resulting solutions were saved for ICP-AES and ICP-MS analysis. The coal was washed at least five times with distilled water, using an ultrasonic cleaner to remove the solvent. After removing the solvent and drying the residual solid, about 0.5 g of this material was removed from each tube for INAA, and CVAA analysis for Hg.

Chemical data for the leachates and residues were processed to derive the percentages of each element leached by each of the four leaching agents. The calculated percentages were then used as an indirect estimate of the modes of occurrence of specific trace elements in the coals. These results were determined for 44 elements. By comparing data for the residual fractions with data for the solutions, we estimate a relative error of up to ±20 percent and an absolute error of ±10 percent, for the leached percentages reported.

Scanning Electron Microscopy

Coal-epoxy pellets were prepared for SEM and electron microprobe analysis following the ASTM D2797-85 technique for anthracite and bituminous coal (ASTM, 1993). The casting procedure impregnates, under pressure, about 7-8 grams of crushed coal sample with epoxy. The coal-epoxy mixture is poured into a mold, cured overnight at 60 °C. and ground on a 15 μm diamond platen and 600- grit SiC paper until flat and smooth. Rough polishing is done with 1 μm alumina and final polishing is completed with 0.06 μm colloidal silica. Ultrasonic cleaning between and after the various steps insures a final product free of extraneous abrasive material.

Polished pellets were examined using a JEOL 840[1] or an ETEC Autoscan[1] scanning electron microscope equipped with an energy-dispersive detector (EDX). Mineral identifications are assigned on the basis of morphology, and major-element composition of grains. Both secondary electron imaging (SEI) and back-scattered electron imaging (BSE) modes were used in coal sample characterization. EDX analysis provided information on elements having concentrations at the tenths-of-percent level or greater. Typical operating conditions for scanning microscopy are: accelerating potentials of 10-30 kV, magnifications of ~50->10,000 times and working distances of 15 or 39 mm (JEOL) or 15 to 20 mm (ETEC).

Electron Microprobe Analysis

A fully-automated, five spectrometer JEOL JXA 8900L Superprobe[1] was used to quantitatively determine element concentrations in sulfides by the wavelength-dispersive technique. The following elements were measured: Fe, S, Se, Cu, Ni, As, Zn, Cd, and Co. Natural and synthetic standards were used. Beam current used was 3.0 $\times 10^{-8}$ amps; accelerating voltage was 20 KeV. A minimum beam diameter of about 1-3 micrometers was attained, limiting the minimum grain size for analysis to about 10 micrometers. With the exception of Co, a minimum detection limit of about 100 ppm (0.01 wt. %) was attained for each of the trace elements analyzed in pyrite, using counting times of 60 seconds for peak positions and 30 seconds for upper and lower backgrounds. For Co, the minimum detection limit in pyrite is 500 to 600 ppm (0.05-0.06 wt. %), due to an interference with Fe K_β.

X-ray diffraction analysis

To obtain semi-quantitative information on the minerals present in the study coals, samples of low-temperature ash (LTA) were pressed into pellets and analyzed using an automated X-ray diffractometer. The X-ray signals were scanned over an interval from 4 to $60^\circ\ 2\theta$. Counts were collected at an interval of 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).

Results

Bulk analytical results (Appendix 1) will ultimately provide a direct inter-laboratory comparison of coal analytical methods. Additionally, these data are the basis for our leaching studies, as the percentages reported in the leaching process express the fraction of the bulk value removed at each step. Bulk chemical data for

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[1] Use of trade names is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey

each of the three project coals, given in Appendix 1, show results from each of the participating laboratories available to date. Because the data are considered preliminary and are generally not published we have not included the names of the laboratories except for our own data. The data is determined by 10 different techniques including ICP-AES (ICP), ICP-MS, spark source mass spectroscopy (SparkMS), CVAA, atomic fluorescence spectrometry (AFS), HGAA, INAA, PIXE, graphite furnace atomic absorption analysis (GFAA) and classical flame atomic absorption analysis (AA). Considering the variety of techniques used, the agreement is generally good. Excluding data obtained by proton induced X-ray emission (PIXE; Column E, Appendix 1), the best agreement was found for Ga, Li, Rb, Sc, Mn, and Ba. For each of these elements, agreement, expressed as the percentage range of total deviation, is within 15 percent for all three coal samples. A large group of elements, including As, Be, Cr, Cu, Ga, Ge, Li, Mo, Nb, Ni, Pb, Sb, Sr, Th, Tl, U, V, Se, Cs and B (excluding the one anomalous Se, Cs, and B value for Gascoigne-Wood #2) have deviation ranges no worse than 40 percent in any of the three coals (excluding PIXE data in column E). Mercury values are within ±40 percent except for the Wyee coal sample. Cobalt was only within ±40 percent for the Gascoigne Wood #2 sample and Y was only within ±40 percent for the Wyee sample. For Zn (1-75%) the agreement is poor for each of the three coals and Cd had poor agreement for two coals and only one value above the detection limit for the third coal sample. For Hg and Cd, this is a function of the low concentration levels and large uncertainties as detection limits are approached. Where at least 3 values are reported for a given element, USGS data generally fall within the range of the others, or deviate from this range by no more than about 20 percent (Appendix 1A-1C). Element mode of occurrence (leaching) results were not obtained for B, Si, Ga, Ge, and Nb. Inclusion of bulk data for these elements in Appendix 1A-1C is primarily for the purpose of comparing our results with those of other laboratories. No two laboratories used the same procedure to analyze their samples. The procedures used for each element are reported in Appendix 1A-1C.

Comparing the USGS values for the three coals (Appendix 2), it is evident that the Wyee sample is enriched in trace-elements normally associated with carbonates (e.g. Mn >250 ppm; Sr >100 ppm), whereas the Gascoigne-Wood #2 has above-average concentrations of several transition metals, including Co (6 ppm), Cu (30 ppm), Ni (19 ppm), V (47 ppm) and Cr (35 ppm). The Illinois #6 sample is enriched in B (229 ppm), a result of marine influence, and contains 3-5 times the Zn of the other coals (71 ppm), consistent with the presence of sphalerite.

Mineralogy of the project coals is summarized in Appendices 3 and 4. Semi-quantitative estimates of bulk mineralogy are given in Appendix 3, based on x-ray diffraction (XRD) of low temperature ash (LTA). The percentage of clay in the LTA for the three samples ranges from 55 percent to 75 percent (7.3-14.1 on a whole coal basis). The Gascoigne Wood #2 LTA has the largest percent of clay, with 35 percent illite, 30 percent kaolinite and 10 percent chlorite, but the Wyee has the highest percent on a whole coal basis due to its higher ash content. Illite, as determined by XRD, is defined by the peak at 100 Å and may include mixed layered clays. The

Illinois #6 and Wyee LTA have similar amounts of illite (10-20%), and kaolinite (35-45%), and both samples lack chlorite. The percentages of quartz in the LTA are about 25 percent for each sample. There is a large range in the pyrite content of the samples. The Wyee LTA has little or no pyrite, whereas a pyrite content of 15 percent was determined for the Illinois #6 LTA. Small amounts of pyrite were found in the Wyee coal by SEM/EDX. Iron in the Wyee coal was found to be present mostly in siderite/carbonates rather than pyrite. Pyritic sulfur values for the 3 coals range from 0.02 percent in the Wyee to 1.39 percent in the Illinois #6, which translates into 0.04 to 2.6 weight percent pyrite in the whole coals.

SEM examination of the three coals reveals a wide range of accessory phases in the Gascoigne-Wood #2 and Wyee coals, and a fairly simple mineralogy for the Illinois #6 sample (Appendix 4). These results are used in interpreting the leaching data, in the sections describing the results for each element.

Interpretation of Leaching Data

Leaching results are plotted for each element in Figures 1 to 10. Each graph shows the leaching steps in sequential order for each coal. The graphs show the percent of each element removed at each step and the cumulative percent leached. Interpretation of the results is considered in the section that follows.

For each element in each coal, data for four leachate fractions are generated (Figs. 1-10). The four leachates are intended to reveal as much as possible about the mode of occurrence of elements in coal. The leachates were chosen specifically to attack the most commonly occurring inorganic parts of coal. The ammonium acetate leach removes loosely bound ions that may be organically associated or ions absorbed on clays, prior to attack by the other reagents. The HCl-leaching step attacks carbonates, such as calcite, and monosulfides such as chalcopyrite, sphalerite, and galena. The HF-leaching step attacks silicates, including quartz and clay minerals. Note that some silicates, such as zircon, may be resistant to HF-leaching. Leaching with HNO_3 primarily attacks disulfides such as pyrite, giving an indication of which elements are pyrite-associated, and their proportions. Because the sum of these four leaching steps is seldom 100 percent, by taking the difference from 100 percent, the leaching process indirectly gives information on elements associated with insoluble minerals such as zircon and chromite and the organic portions of coal that remain in the solid residue after leaching. These general principles should allow the researcher to make some interpretations based solely on the proportions of these five leaching fractions. In practice we incorporate the leaching data with data from XRD, SEM/EDX, and microprobe in making mode of occurrence determinations. Data obtained by XRD are used to determine the relative amounts of major and minor minerals in the coal samples. Electron microprobe gives quantitative elemental concentrations of specific mineral grains. SEM/EDX, and electron microprobe, are used to identify minor and trace minerals. With this information mass balances are calculated by knowing the major and minor constituents of the major minerals and the major constituents of minor and trace mineral phases. Our final interpretations include our leaching results, the mass balance information, geochemical principles, and experience obtained from previous leaching experiments. Our interpretations of element mode of occurrence in the three coals are summarized below in Table 2. Similar results are given by Querol et al. (1998) based on a synthesis of the USGS data set and results reported by Querol and Huerta (1998).

Table 2: Interpretations of modes of occurrence (Except column 1 units of all numbers are in %). Results generally agreed with Querol and Heurta (1998) and Huggins (1998) except as noted.

#	Element	Wyee	Gascoigne Wood	Illinois #6
1.	Li	75 Al-silicate	80 Al-silicate	75 Al-silicate
2.	Be[1]	Al-silicate/organic	Al-silicate/organic	Al-silicate/organic
3.	Al	90 Al-silicate	90 Al-silicate	90 Al-silicate
4.	Na[2]	30 Al-silicate 50 exchangeable	25 Al-silicate 45 exchangeable	30 Al-silicate 45 exchangeable
5.	K	90 Al-silicate	90 Al-silicate	90 Al-silicate
6.	Rb	50 Al-silicate 35 uncertain	25 Al-silicate 65 uncertain	70 Al-silicate 15 uncertain
7.	Cs	20 Al-silicate 45 uncertain 25 exchangeable	15 Al-silicate 75 uncertain	60 Al-silicate 20 uncertain
8.	Mg[3]	50 carbonate 20 Al-silicate	25 carbonate 30 Al-silicate	15 carbonate 50 Al-silicate
9.	Ca	80-100 carbonate	75-80 carbonate 20-25 organic	70-75 carbonate 25-30 organic
10.	Sr	organic, carbonate, Al-silicate, phosphate	Organic, carbonate, Al-silicate, phosphate	Organic, carbonate, Al-silicate, phosphate
11.	Ba	Barite	Barite	Barite
12.	Sc	50 organic 30 Al-silicate	30 organic 65 Al-silicate	25 organic 65 Al-silicate
13.	Ti	Ti-oxides and/or Al-silicates	Ti-oxides and/or Al-silicates	Ti-oxides and/or Al-silicates
14.	V	70 organic 25 Al-silicate	45 organic 55 Al-silicate	35 organic 60 Al-silicate
15.	Cr	60 organic 35 Al-silicate	40 organic 50 Al-silicate 10 chromite	65 organic 35 Al-silicate

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[1] Querol and Heurta (1998) found nearly all Be in all coals organically associated.

[2] Querol and Heurta (1998) found Wyee: 20% organic and 80% Al-silicate; Gascoigne Wood #2:45%zeolite, 55% Al silicate; Illinois #6: 25% ionic, 45% organic and 30 % Al silicate.

[3] Querol and Heurta (1998) found Wyee: 100 % Carbonate; Gascoigne Woods #2: 97% carbonate; 3% organic; Illinois #6 20% organic and 80% Al-silicates.

Table 2 (continued): Interpretations of modes of occurrence (Except column 1 units of all numbers are in %). Results generally agreed with Querol and Heurta (1998) and Huggins (1998) except as noted.

#	Element	Wyee	Gascoigne Wood	Illinois #6
16.	Mn	up to 85 carbonate 10 organic	up to 80 carbonate 20 Al-silicate	up to 60 carbonate 20 sulfide 15 Al-silicate
17.	Fe	80 siderite	35 siderite, 35 silicate 30 pyrite	75 pyrite 10-15 carbonate
18	Co	75 organic	Organic, Al-silicate, sulfide, carbonate in subequal amounts	Organic, Al-silicate, sulfide, carbonate in subequal amounts
19.	Ni	35 organic, 30 Al-silicate; rest is subequal sulfide, carbonate	45 organic 20 Al-silicate 20 carbonate	30 sulfide, 35 organic; rest is subequal Al-silicate, carbonate
20.	Cu	35 organic 25 Al-silicate 35 pyrite/chalcopyrite	35 pyrite/chalcopyrite 50 organic 15 Al-silicate	70 pyrite/chalcopyrite 10 Al-silicate
21.	Zn[4]	Mainly sphalerite; Rest is Al-silicate	Mainly sphalerite rest is organic, Al-silicate, pyrite	Mainly sphalerite; rest is organic, pyrite
22.	Mo[5]	30 organic 25 Al-silicate 10 sulfide	30 organic 40 Al-silicate 15 sulfide	50 organic 35 Al-silicate 10 sulfide
23.	Cd	Sphalerite, organic	Sphalerite	Sphalerite
24.	As	35 sulfide	55 sulfide	40 sulfide
25.	Se[6]	45 organic 25 sulfide	50 sulfide 35 organic	70 sulfide 25 organic
26.	Sb	75 organic 15 Al-silicate 10 sulfide	50 organic 25 sulfide 15 silicate	50 organic 25 sulfide 20 Al-silicate
27.	Hg	Mostly sulfide	Dominantly sulfide	Dominantly sulfide
28.	W	40 organic/W-oxides 30 Al-silicate/W-oxides	50 organic/W-oxides 20 Al-silicate/W-oxides	55 organic/W-oxides 45 Al-silicate/W-oxides
29.	Tl	45 Al-silicate 30 organic 25 sulfide	65 sulfide 25 Al-silicate	45 sulfide 20 organic 20 Al-silicate
30.	Pb	55 galena, 15 pyrite, PbSe	60 galena 25 pyrite, PbSe	45 galena 40 pyrite

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[4] Huggins (1998) found Wyee: organic dominate; Gascoigne Wood #2: illite is the dominate mode of occurrence.

[5] Querol and Heurta, (1998) did not find an Al silicate fraction in any of the coal samples.

[6] Gascoigne-Wood #2: Querol and Heurta (1998) 100% pyrite; Huggins (1998) only minor pyrite.

Table 2 (continued): Interpretations of modes of occurrence (Except column 1 units of all numbers are in %). Results generally agreed with Querol and Heurta (1998) and Huggins (1998) except as noted.

#	Element	Wyee	Gascoigne Wood	Illinois #6
31.	Hf	Dominantly zircon	Dominantly zircon	Dominantly zircon
32.	Ta	65 Oxide 25 Al-silicate	65 Oxide 15 Al-silicate	65 Oxide 25 Al-silicate
33.	Th	Mainly phosphates, oxides, organics	Mainly phosphates, oxides	Mainly phosphates, oxides
34.	U	45 organic and/or zircon 30 Al-silicate	40 organic and/or zircon 40 Al-silicate	75 organic and/or zircon
35-6	Y/HREE	Phosphates, organics	Phosphates, organics	Phosphates, organics
36.	LREE	Phosphates	Phosphates	Phosphates

In the sections that follow, results for each element are discussed, largely in order of atomic number with exceptions to allow for grouping of elements that are geochemically similar. For convenience, elements are also shown in this order in Table 2 and in Figures 1 to 10. In order to facilitate moving between the text, Table 2, and figures, each element is assigned a number representing the order in which it is discussed.

1) Lithium (Li)

In all three coals, HF removed 75 to 80 percent of the Li (Fig. 1a). This indicates that a large part of the Li is in silicates, primarily clay minerals such as illite. The remaining 20 to 25 percent of the Li was not leached and may be associated with the organic fraction.

2) Beryllium (Be)

Beryllium results show a 50 to 80 percent HF-leachable fraction, indicating that this portion of Be is in silicates (Fig. 1b). Up to 40 percent of the Be is unleached, and is probably associated with organics. In contrast, Querol and Heurta (1998) found that nearly all of the Be in the three coals is associated with organics. The results of Querol and Heurta (1998) may be explained if organically bound Be is attacked to some extent by HF. Additionally, because of its atomic weight and/or low abundance, Be can be difficult to analyze, possibly leading to the conflicting results.

3) Aluminum (Al)

Aluminum was leached only by HF (Fig. 1c). Ninety percent of the Al in all three coals was leached by HF, clearly indicating that this element resides in silicates. Aluminum is an essential structural constituent in the clay minerals illite and kaolinite, as well as in feldspars, major components of the LTA of all three samples (Appendix 3). The unleached 10 percent of the Al may be insoluble or shielded components or may be organically associated.

4) Sodium (Na)

All three coals have similar leaching patterns, with significant fractions of Na removed by each leaching agent (Fig. 2a). About 50 percent of the Na in each coal was removed by ammonium acetate. We believe that this exchangeable portion of the Na is in ionic form (Na^+). The next most abundant mode of occurrence (30%) is in the HF-leachable (silicate) fraction. There are also small amounts of HCl-soluble (5-15%) and HNO_3-soluble (10-15%) Na. Results obtained by the USGS differ somewhat from those of Querol and Huerta (1998), who find a 20 percent organic/80percent aluminosilicate Na distribution for the Wyee, a 25 percent ionic/45 percent organic/30 percent aluminosilicate distribution for the Illinois #6, and a 45 percent zeolite/55 percent aluminosilicate Na distribution for the Gascoigne-Wood #2. The reason for this disagreement is currently under investigation.

5) Potassium (K)

There was good agreement for K leachability among the three coals, with 90 percent leached by HF indicating the presence of K in the silicates (Fig. 2b). This leaching behavior is exactly like that of Al and similar to that of Li (Figs. 1-2). The remaining unleached 10 percent may be organically associated. While the fraction of K leached by HF is identical in each of the three coals, the bulk K_2O content varies from about 0.2 to 0.6 percent, on a whole-coal basis. The amount of illite indicated by XRD appears to vary accordingly (when calculated on a whole-coal basis), suggesting that K is incorporated in illite or mixed layer clays.

6) Rubidium (Rb)

Rubidium was leached primarily by HF (25-70 %) and by HNO_3 (15-65 %; Fig. 2c). Leaching totals for Rb for all three coals are above 85 percent. For the Illinois #6 coal, the HF-leachable Rb fraction is 70 percent, indicating that the bulk of the Rb is in silicates, probably illite and mixed layer clays. For the Wyee coal, HF-leachable Rb is the dominant form (50 %), but a significant HNO_3-leachable Rb

(35%) was also found. In the Gascoigne-Wood #2, the fraction of HNO_3-leachable Rb (65%) is greater than that of HF (35%). The mode of occurrence of HNO_3-leachable Rb is unclear.

7) Cesium (Cs)

Leaching patterns for Cs are similar to those for Rb except for the presence of a 5-25 percent fraction of ammonium-acetate-leachable Cs that was not found for Rb (Fig. 2d). The sum of the ammonium acetate and HCl leaching steps for Cs ranges from 10 percent (Gascoigne-Wood #2) to 30% (Wyee), whereas for Rb, no ammonium acetate-leachable material was found. Only the Wyee had HCl-leachable material (5%). For the Illinois #6 coal, the behavior of Cs is similar to that of Rb, with a large (60 %) HF-leachable portion in silicates, and a smaller (20%) HNO_3-soluble amount. The Wyee coal has 45 percent of its Cs in an HNO_3-soluble phase and a 20 percent fraction in HF-leachable silicates. In the Gascoigne-Wood #2 coal, the dominant mode of occurrence for Cs is the HNO_3-soluble phase (75%), with only 15 percent of the Cs in silicates. Like Rb, the mode of occurrence for HNO_3-leachable Cs is unclear.

Leaching totals for Cs are all 95 percent or above. The fraction of organically associated Cs must therefore be small; however, some Cs may be present as exchangeable ions, especially in the Wyee.

8) Magnesium (Mg)

Leaching data for Mg indicate two major modes of occurrence, in silicates and carbonates, but the data are not as clearly defined as that for some other elements. HF-leachable (silicate-bound) Mg ranges from 20 percent (Wyee) to 50 percent (Illinois #6) among the three coals (Fig. 3a). Leaching totals for each of the coals are in the 70-75 percent range, limiting the organic Mg fraction to about 30 percent. For the Wyee coal, the HCl-leachable fraction (50%) is larger than the silicate fraction (20%), indicating that Mg exists primarily in carbonates. Smaller (5-20%) HCl-leachable fractions were found in the other two coals. All 3 coals have a small HNO_3-soluble fraction, which is most abundant (15%) in the Gascoigne Wood #2. Overall, the leaching data indicate that Mg resides primarily in silicates (illite) in the Illinois #6, and carbonates in the Wyee. The Gascoigne-Wood #2 shows evidence of both modes of occurrence, with the silicate fraction being dominant. Querol and Heurta (1998) find an 80 percent aluminosilicate association for Mg in the Illinois #6 sample and a 100 percent carbonate association for Mg in the Wyee. Their data does not indicate a silicate association for Mg in the Gascoigne-Wood. These differences are currently under investigation.

9) Calcium (Ca)

For each of the 3 coals, the ammonium acetate and HCl fractions dominate leaching data for Ca, but the sum of these fractions is only in the 55-60 percent range (Fig. 3b). Calcite is soluble in HCl, and partially soluble in ammonium acetate as shown by Palmer et al. (1998). The sum of these two fractions is an indication of the proportion of Ca contained in calcite or other carbonate minerals.

Previous leaching tests for a different sample of the Illinois # 6 (Palmer et al., 1993; Finkelman et al., 1990) have given totals of about 80-90 percent. Based on comparison with previous results, we consider the low totals to be the result of incomplete leaching in these samples rather than the presence of a large organically bound Ca fraction. A strong carbonate association for Ca was found by Querol and Huerta (1998), ranging from 71 percent in the Illinois #6 sample to 100 percent in the Wyee. We are currently investigating possible causes for incomplete dissolution of Ca.

10) Strontium (Sr)

Strontium was removed from each of the coals by all four leaching agents with total percentages leached ranging from 65 percent (Illinois #6) to 85 percent (Wyee; Fig. 3c). This leaching behavior indicates that Sr occurs in several phases and there is no dominant mode of occurrence. Possible modes of occurrence for Sr include the organic fraction, carbonate, aluminosilicate and phosphate phases. Multiple modes of occurrence for Sr are inferred by Querol and Huerta (1998) who found carbonate, silicate and organic associations for Sr in the Illinois #6, and Gascoigne-Wood samples, and carbonate and aluminosilicate associations for Sr in the Wyee.

Phosphates were found using the SEM/EDX, especially in the Wyee coal. For example, the phosphate mineral gorceixite (Ba Al_3 $(PO_4)(P)_3OH)$ $(OH)_6$), which may contain Sr in solid solution, was found in the Wyee coal, attached to a grain of sphalerite (Fig. 11).

11) Barium (Ba)

Like Sr, all four leaching agents (Fig. 3d) leached Ba from each of the three coals. Unlike Sr, we consider the leaching behavior of Ba to be controlled by a single dominant phase (barite), rather than as a minor element in multiple phases. Barite was observed in each of the coals (Appendix 4) and is especially common in the Gascoigne-Wood #2.

Although barite is generally assumed to be insoluble, solubility data (Linke 1959) indicate that a few ppm of Ba could be dissolved from barite at by solvents used in our leaching process. Based on barite solubility data for the leaching solutions at or near room temperature, the amount of Ba in solution after the ammonium acetate HCl, and HNO_3 leaching steps is consistent with dissolution of barite. Fifty to fifty-five percent of the Ba in each of the coals was leached by HF; solubility data for barite in HF are not available. We are examining barite solubility under our leaching conditions for all solvents but the data are not yet available and we do not yet know if some of the Ba is associated with the clays.

12) Scandium (Sc)

Scandium was found to be leachable by HCl and HF only, with totals ranging from 50 percent (Wyee) to 75 percent (Gascoigne-Wood #2; Fig. 4a). The HF-leachable fraction is greater than the HCl fraction in each of the coals. The Illinois #6 and the Gascoigne Wood #2 each have 65 percent HF-leachable Sc in silicates, and 25 to 30 percent unleached Sc associated with organics. The Wyee coal has a larger (50%) fraction of organic-associated Sc and only 30 percent in the silicates. The subsidiary HCl-leachable form of Sc found for each coal ranges from only 5 percent in the Illinois #6 to 20 percent in the Wyee.

13) Titanium (Ti)

All three coals had 70 to 80 percent of their Ti leached by HF (Fig. 4b). We interpret the dominant mode of occurrence of Ti to be as Ti oxides, which have been observed in the Wyee and Gascoigne-Wood #2 samples, and in the Illinois #6 coal by Dehmer et al. (1998). The leaching data suggest that Ti-oxides are partly soluble in HF, but some Ti may also be present in solid solution in clay minerals such as illite. The leaching data do not distinguish these two possible modes of occurrence, however, based on density separations, Querol and Huerta (1998) found that up to 25 percent of the Ti in the three coals is present in the aluminosilicate fraction. Some of the Ti in this fraction may also occur as fine-grained (1-2 micrometer) inclusions of TiO_2 in clay minerals rather than as Ti in solid solution. Huggins (1998) found that titanium has three primary modes of occurrence in different proportions in the three coals: as Ti-oxides, as Ti in illite, and as Ti in the organic fraction, possibly present as nano-scale TiO_2.

14) Vanadium (V)

The behavior of V is similar to that of Sc in the three coals (Fig. 4c). Like Sc, V was only leached by HF (25-55%) and HCl (0-5%). Also, like the results for Sc, there are large fractions of unleached V, ranging from 35 percent in the Illinois #6, to 70 percent for the Wyee. The data for V show that silicate and organic modes of occurrence are dominant. The large organic-associated V fraction found for the Wyee (up to 70%) is similar to that found for Sc (up to 50%), Cr (up to 60%), and Co (up to 75%), showing a greater tendency for organic association of elements in the Wyee relative to the other two coals.

15) Chromium (Cr)

Like V, Cr shows large (40-65) percents of unleached element, indicating significant organic fractions (60-65% in Wyee and Illinois #6; Fig. 4d). The HF fraction is again the next most abundant, ranging from 35 percent for the Wyee and Illinois #6, to 50 percent for the Gascoigne-Wood #2. The 50 percent silicate Cr fraction found for the Gascoigne-Wood #2 is consistent with XAFS (XANES) data of Huggins (1998) that indicates a large part of the Cr in this coal is associated with illite. Some of the unleached Cr could be insoluble chromite rather than Cr in the organics. Chromite was observed in the Illinois #6 and Wyee samples.

16) Manganese (Mn)

Carbonates were found to be the dominant mode of occurrence for Mn in each of the three coals investigated. This mode is indicated by the sum of HCl and ammonium acetate fractions (see discussion for Ca), which ranges from 60 percent (Illinois #6) to 85 percent (Wyee; Fig. 5a). Some of the ammonium acetate-leachable Mn may be loosely-bound ions in the organic matrix rather than Mn in carbonates. These data show that the Wyee coal has up to 85 percent Mn in carbonates, with small amounts of Mn in silicates and organics. The Gascoigne-Wood #2 sample has up to 80 percent Mn in carbonates, and 20 percent in silicates (probably illite). The Illinois #6 has up to 60 percent Mn in carbonates, 15 percent in silicates, and 20 percent in sulfide associations, probably pyrite.

17) Iron (Fe)

Leaching data indicate 3 distinct occurrence patterns for Fe in the 3 project coals (Fig. 5b). The Wyee coal has an 80 percent HCl-leachable fraction, indicating a carbonate association for Fe. A subsidiary (15%) silicate association is also indicated, probably Fe in illite, or in mixed-layer clays. No pyritic Fe is indicated for the Wyee sample, consistent with SEM, XRD, and pyritic sulfur results showing that the pyrite content of this sample is very low. While the large HCl-leachable fraction indicates a carbonate association for Fe in the Wyee, the lack of corresponding ammonium acetate-leachable Fe suggests that the carbonate host is siderite or another Fe-rich carbonate, rather than calcite. The presence of siderite in the Wyee is confirmed by SEM/EDX, and by Mössbauer spectra (Huggins, 1998). For the Gascoigne-Wood #2 sample, 3 sub-equal modes of occurrence were found. Thirty-five percent HF and HCl-leachable fractions show that Fe is present in silicates and carbonates, respectively. An additional 30 percent fraction leached by HNO_3 shows the proportion of Fe in pyrite. For the Illinois #6 sample, the 75 percent fraction of Fe in pyrite is consistent with the abundance of pyrite in this sample. Leaching totals for Fe are 95-100 percent for each of the three coals, showing good mass balance, and little or no organic association.

18) Cobalt (Co)

Leaching data for Co are suggestive of multiple modes of occurrence, but leaching totals are quite variable (Fig. 5c). Leaching totals in the Wyee are only 25 percent, suggesting that up to 75 percent of the Co is associated with organics. The other two coals have minor HF- and HNO_3-leachable Co, and up to 30 percent associated with organics. In each of the three coals, Co is also present in a HCl soluble phase, possibly a carbonate or monosulfide, ranging from 10 percent (Wyee) to 40 percent (Gascoigne Wood #2).

19) Nickel (Ni)

Nickel was removed in nearly every step of our leaching process (Fig. 5d). For the Wyee coal, a 30 percent Ni fraction is in the silicates and up to 35 percent is associated with organics. Smaller amounts of Ni are associated with sulfides and carbonates in the Wyee. The Gascoigne-Wood #2 and the Illinois #6 are similar in having up to 35-45 percent of the Ni associated with organics, 20 percent in a HCl soluble phase and 15 to 20 percent in silicates. The Illinois #6 has twice the amount of nickel in the sulfide fraction (30%), compared to the Gascoigne-Wood #2 (15%).

The presence of Ni in pyrite is confirmed by electron microprobe (Appendix 5), and summarized as follows: For the Gascoigne-Wood #2 sample, Ni contents in pyrite range from below the detection limit (<100 ppm), to about 0.20 weight percent. An average Ni concentration of 270 ppm (0.027 wt. %) was determined based on 67 pyrite analyses. Using this average concentration, and a pyrite content of 0.7 weight percent (calculated from the pyritic sulfur value), about 10 percent of the Ni in the Gascoigne-Wood #2 coal can be accounted for by pyrite. This estimate is in good agreement with the15 percent fraction of Ni in pyrite determined by leaching with HNO_3.

For the Illinois #6 coal, microprobe data indicate a concentration range from below the detection limit (<100 ppm) to a maximum of 0.06 weight percent. Typical values are in the 0.00 to 0.02 weight percent range. The probe data are in good agreement with the leaching results, which would require an average Ni concentration in pyrite of about 145 ppm (0.015 wt. %) in order to account for the 30 percent fraction of Ni in pyrite determined by leaching. Pyrite was not sufficiently abundant in the Wyee coal to obtain a representative microprobe analysis, but semiquantitative EDX analysis indicates that some Ni is present in Wyee pyrite.

20) Copper (Cu)

Each of the three coals has Cu removed by HCl, HF and HNO_3 in amounts of 10 percent or greater (Fig. 6a). The Wyee and the Gascoigne-Wood #2 also have large (35-50 %) amounts of unleached, organic-associated Cu. For the Wyee coal, the 25 percent HCl-leachable fraction is likely to be associated with chalcopyrite, as confirmed by SEM/EDX observation. Smaller HCl-leachable fractions were found for the Gascoigne-Wood #2 and Illinois #6 coals. The Illinois # 6 sample shows a significant (60%) fraction of Cu in pyrite. Electron microprobe analysis shows the Cu content of pyrite in the Gascoigne-Wood #2 (below detection limit to 0.10 wt. %) and Illinois #6 (below detection limit to 0.08 wt. %) to be similar, but pyrite is much more abundant in the Illinois #6 sample.

21) Zinc (Zn)

Like Cu, $\geq$10 percent fractions of Zn were removed by HCl, HF, and HNO_3. Unlike data for Cu, leaching totals for Zn are each $\geq$ 80 percent, indicating smaller organically associated fractions (Fig. 6b). Based on SEM/EDX observation, we consider sphalerite, which is present in all three coals, to be the dominant mode of occurrence for Zn. As such, we would expect large HCl-leachable fractions for Zn. Surprisingly, these fractions are only in the 20-25 percent range. Illite and pyrite associations are other possible modes of occurrence for Zn indicated by the leaching data. The presence of minor amounts (< 0.01 to 0.04 wt. %) of Zn in pyrite of the Illinois #6 and Gascogne-Wood #2 samples is indicated by electron microprobe analysis (Appendix 5). However, the 45 percent fraction of Zn in pyrite indicated for the Illinois #6 coal would require an average Zn content of pyrite in excess of 0.14 weight percent, inconsistent with the microprobe data. Likewise, for the Gascoigne-Wood #2, the 25 percent fraction of Zn in pyrite indicated by the leaching data would require an average Zn content of pyrite approaching 0.10 weight percent. Possible explanations for the Zn leaching data include shielding of sphalerite by organics and/or partial solubility of residual sphalerite in HNO_3 (and HF as well).

XAFS (XANES) data (Huggins, 1998) indicate a 75 percent fraction of Zn in sphalerite for the Illinois #6 samples he studied, however, he considers illite and organic (possibly carboxyl) associations to be the dominant modes of occurrence of Zn in the Gascoigne-Wood #2 and Wyee coals, respectively.

22) Molybdenum (Mo)

Leaching data for Mo show multiple modes of occurrence, with silicate (25-40%) and organic (up to 35-50%) fractions the dominant associations, and subsidiary HNO_3-soluble Mo (10-15%; Fig. 6c). A large (25%) ammonium acetate-leachable fraction was found for the Wyee coal; if this exchangeable Mo is associated with organics, this proportion could be added to the unleached fractions, giving up to 55 percent organically-associated Mo in both the Wyee and Illinois #6 samples. Density separations (Querol and Heurta, 1998) show a strong organic association for Mo, and for the Gascoigne-Wood #2 and Illinois #6, a subsidiary pyrite association is also indicated. The density separations do not show the silicate fraction indicated by leaching.

23) Cadmium (Cd)

Results of SEM/EDX show that Cd is present in sphalerite in the Gascoigne Wood #2 coal, however, because the amount of Cd in the whole coal is at or below the detection limit, no leaching data were obtained for this sample. For the Wyee coal, cadmium was removed at every step of the leaching process (Fig. 6d). The primary modes of occurrence in the Wyee are a 30 percent HCl-soluble phase (sphalerite) and up to 50 percent Cd associated with organics. The Illinois #6 coal has a 45 percent HNO_3-leachable Cd fraction, the same proportion indicated for Zn in this coal. We consider the fraction of Zn and Cd in "pyrite" (probably sphalerite) indicated by the leaching data to be over-represented. Likewise, the proportion of HCl-leachable Cd in the Illinois #6 coal seems too low, only 20 percent, indicating that no more than 20 percent of Cd is in sphalerite (see discussion for Zn). An additional 30 percent (or less) fraction of organically associated Cd is indicated by unleached Cd in the Illinois #6 sample. This data could be explained by the presence of sphalerite in pyrite but we did not see this in the samples. Many of the Cd values are near the detection limit leading to a large uncertainty for many of the Cd values.

24) Arsenic (As)

Leaching data indicate a 35 percent (Wyee) to 55 percent (Gascoigne Wood #2) fraction of arsenic in pyrite, and a 25-40 percent fraction of unleached As, inferred to be organically-associated (Fig. 7a). Lesser amounts of HF- (10-20%) and HCl- (10-15%) leachable As were determined in each of the three coals. The portion of HCl-leachable As corresponds well to the 15 percent fraction of arsenate (AsO_4^{3-}) found by Huggins (1998) for each coal using XAFS (XANES). Arsenate is generally considered to form by oxidation of arsenic-bearing pyrite. The XAFS data give somewhat smaller organic As fractions than the USGS data (0 for Gascoigne Wood #2, < 10 percent for Illinois #6), suggesting that some of the unleached As, especially in the Illinois #6, may actually be in pyrite that was not completely digested, perhaps due to shielding by organic matter. For the Wyee, there is good agreement between the leaching and XAFS data for each of the major As fractions-pyrite, organic, and arsenate.

The presence of As in pyrite is confirmed by electron microprobe (Appendix 5), and summarized as follows: For the Gascoigne Wood #2 sample, As in pyrite ranges from below the detection limit (<100 ppm), to nearly 2 weight percent. An average As value of 0.13 weight percent gives sufficient As to account for all the As in the Gascoigne Wood #2, based on a pyrite content of 0.7 percent (calculated from the pyritic sulfur content), and a whole-coal As value of 9 ppm (Appendix 1-2). An average As content of about 0.2 weight percent was determined for the Gascoigne-Wood pyrite, based on 67 microprobe determinations.

For the Illinois #6 coal, microprobe data indicate As contents in pyrite ranging from below 0.01 weight percent to about 0.04 weight percent. These data are consistent with an average concentration of 115 ppm (0.012 wt. percent), required to account for all of the As (3 ppm), based on a pyrite content of 2.6 weight percent. Pyrite was not sufficiently abundant in the Wyee coal to obtain a representative microprobe analysis.

25) Selenium (Se)

The Gascoigne-Wood #2 and Illinois #6 samples each have a significant fraction of Se associated with pyrite (50% and 70%, respectively; Fig. 7b). The Gascoigne-Wood #2 and Illinois #6 samples each have subsidiary organic associations (35% and 25%, respectively). For the Wyee sample, whole-coal Se values are near the detection limit (0.5 ppm), and results for this sample are less reliable. The Wyee data indicate a 45 percent organic fraction and a 25 percent pyritic fraction for Se. The pyrite and organic associations found for these samples are generally confirmed by other methods, however the proportions indicated are rather variable. For example, XAFS (XANES) data indicate only a minor fraction of pyrite-hosted Se in the Gascoigne-Wood #2 (Huggins, 1998), whereas our results show this fraction to be 50 percent, and density separations (Querol and Heurta, 1998) indicate nearly all of the Se is in pyrite.

26) Antimony (Sb)

Antimony is largely associated with organics, with two of the coals (Illinois #6 and Gascoigne-Wood #2) having equal 50 percent portions of unleached Sb in this fraction (Fig. 7c). For the Wyee sample, which has the most pronounced organic association of the three coals, up to 75 percent of the antimony may be associated with organics, depending on the amount of ammonium acetate-leachable Sb that is organically-associated. Subsidiary modes of occurrence for Sb include a pyrite association ranging from 10 percent in the Wyee to 25 percent in the Gascoigne-Wood #2 and Illinois #6. The silicate fraction accounts for 15- to 20 percent of the Sb in each of the three coals.

27) Mercury (Hg)

Selective leaching data indicate that pyrite is the dominant mineral form containing Hg in the three coal samples in this study. However, because Hg concentrations in the solid residue of the HNO_3 leach are below the detection limit for CVAA, only minimum fractions can be given for Hg in pyrite in the Gascoigne Wood #2 (>40 %) and Illinois #6 (>55 %) coals (these values not shown in Fig. 7d).

For the Wyee sample, a total of only 40 percent of the Hg was leached by all solvents, suggesting that an unleached 60 percent portion of the Hg is organically associated. Because Hg concentrations in pyrite are below the detection limit for electron microprobe analysis, the presence of Hg in pyrite could not be confirmed directly.

A strong association of Hg with pyrite was found by Querol and Heurta (1998), for the Gascoigne Wood #2 and Illinois #6 coals, and an association with the heavy mineral fraction was found for the Wyee coal. Taken together with the leaching data, and based on our experience with other coals, a strong pyritic association is indicated for Hg. However, the Wyee coal contains very little pyrite (0.02 % pyritic sulfur), indicating that significant amounts of Hg are organically associated. The association of Hg with the heavy mineral fraction in the Wyee coal (Querol and Heurta, 1998) suggests that a portion of the unleached Hg may be contained in heavy minerals not dissolved by our procedure.

28) Tungsten (W)

Tungsten is primarily associated with organics or with insoluble tungstates. Leaching totals for W range from 45 percent for the Illinois #6 to 65 percent for the Wyee (Fig. 8a). This unleached fraction could represent organically-bound W, or insoluble tungstates. Each coal also has a significant HF-leachable fraction, ranging from 20 percent for the Gascoigne-Wood #2 to 45 percent for the Illinois #6. The HF soluble fraction could represent W in silicates. HNO_3-soluble W was found in the Wyee (30%) and the Gasoigne-Wood #2 (15%). The Gascoigne Wood # 2 also had 15 percent of its tungsten removed by HCl. It is not known what W species are dissolved by HNO_3 and HCl.

29) Thallium (Tl)

Pyritic, organic, and silicate modes of occurrence are the dominant forms determined for Tl (Fig. 8b). For the Gascoigne-Wood #2, a strong (65%) pyritic association was found, with a subsidiary (25%) silicate association. For the Wyee, Tl in silicates is the most abundant form (45%), followed by organic-associated Tl (up to 30%), and pyritic Tl (25%). For the Illinois #6, a 45 percent pyritic association was determined, followed by equal fractions of Al-silicate (20%) and organic (up to 20%) Tl. Leaching totals for thallium range from 70 percent in the Wyee to 100 percent in the Gascoigne Wood #2.

30) Lead (Pb)

A large (45-60%) HCl-leachable fraction, and a smaller (15-40%) HNO_3-leachable fraction was found for Pb in each of the three project coals (Fig. 8c). These data reflect the primary modes of occurrence for Pb, as monosulfides (galena) and in pyrite, respectively. Galena was observed in the Wyee and Gascoigne-Wood #2 coals using SEM/EDX. Lead selenide (PbSe; HNO_3-leachable) was found in the Gascoigne-Wood #2 and Wyee coals. The large fraction of HNO_3-leachable Pb in the Illinois #6 sample is consistent with the high proportion of pyrite in this sample.

31) Hafnium (Hf)

Leaching data for the Wyee and Illinois #6 coals show a predominance of Hf in the HF fraction (50-60%; Fig. 9a). For the Gascoigne-Wood #2, a smaller (15%) HF-leachable fraction is present, together with a substantial (30%) portion of ammonium acetate-leachable Hf.

Hf is commonly found in zircon in proportions that vary, but typically at a HfO_2/ZrO_2 ratio of about 0.01 (Deer et al., 1966). Zircon is generally insoluble to partially soluble in HF, consistent with low leaching totals (50-60%) for each of the three coals, and the tendency for Hf to be concentrated in the HF fraction.

32) Tantalum (Ta)

The leaching behavior of Ta is similar in each of the three coal samples (Fig. 9b). Leaching totals of only 35 percent were obtained for each sample. These low totals are probably indicative of a large fraction of tantalum in insoluble oxides. Of the 35 percent Ta fraction removed from each coal, an HF-leachable portion (15-25%) and an HNO_3-leachable portion (5-20%) was found in every sample. Of these, HF-leachable Ta is predominant in the Wyee and Illinois #6 coals, whereas in the Gascoigne-Wood #2, the HNO_3 leachable portion is slightly larger (20% vs. 15%). The presence of Ta in clay minerals (Palmer and Lyons, 1996) probably accounts for the HF leachable fractions determined.

33) Thorium (Th)

The behavior of Th is somewhat different in each of the three coals (Fig. 9c). The Gascoigne-Wood #2 shows a 65 percent Th fraction in an HNO_3-soluble phase, and a 25 percent unleached fraction, probably insoluble oxides, phosphates such monazite, or perhaps as organically-associated Th. The Wyee has a 40 percent fraction of HCl-leachable Th, and lesser amounts of HNO_3-leachable (20%), HF-leachable (10%), and insoluble (25%) Th. For the Illinois #6 sample, the largest Th fraction is unleached (50%), indicating a significant portion of this element as insoluble phosphates, organics or oxides. Smaller fractions of Th are indicated in silicates (15%) and an HNO_3-soluble phase (20%) in the Illinois #6 coal. The leaching data for Th differ show those of Hf and U, in which the largest fractions are unleached or leached by HF. This suggests that Th is not controlled by zircon. The source of the HNO_3-leachable Th in the Gascoigne-Wood #2 sample is not known.

34) Uranium (U)

Leaching data for U show large (40-70%) unleached fractions, and a predominance of HF-leachable U (20-40%) in the fractions that are leached (Fig. 9d). The large unleached fractions are indicative of insoluble U-oxides, organically associated U, or zircon. Uraninite was found in the Wyee coal using SEM/EDX. The Gascoigne-Wood #2 has the largest HF-soluble fraction (40%), possibly due to a larger proportion of U in zircon (observed). Additionally, the Wyee coal has an HCl-soluble fraction (20%) and the Gascoigne-Wood #2 has an HNO_3-soluble phase (15%). No U-bearing phase was found in the Illinois #6 sample, possibly indicating that its large unleached U fraction (70%) is organically associated.

35) and 36) Yttrium (Y) and Rare Earth Elements (REE)

Leaching data for Y show distinct mode of occurrence patterns for each of the 3 coal samples (Fig. 10a). In the Wyee sample, sub-equal 20-25 percent portions were found by leaching with HCl, HF, and HNO_3, with the remaining 35 percent of the Y not leached. The 35 percent unleached fraction probably represents organically bound Y. The sum of the HCl and HNO_3 fractions for Y is similar to that determined for the HREE (30-50%), suggesting that the mineral xenotime (YPO_4), a common accessory phase in coal, may be involved. Xenotime is partially soluble in HCl and HNO_3 and is known to concentrate HREE (Mariano, 1989; Fig. 10b).

For the Gascoigne-Wood #2, a 55 percent HNO_3-leachable Y fraction was found, with the remainder as HF-leachable (25 %), HCl-leachable (10%) and unleached (10%). The small unleached fraction indicates that most of the Y is in minerals rather than organics. Like the Wyee sample, the sum of the HCl and HNO_3 fractions for Y (65%) and the HREE (60-70%) are similar. The Illinois #6 sample lacks HNO_3-leachable Y, and instead, consists of an HF-leachable fraction similar to the portion found in the other coals (25%), and a large (75%) unleached portion indicating a strong organic association for Y.

Leaching data for the REE show a great deal of continuity as a result of a progressive increase in their organic association with increasing atomic number (Fig. 10). For the light rare earths, leaching totals exceed 80 percent, indicating a strong association with mineral phases such as monazite (seen in Wyee, and in Illinois #6 by Dehmer et al., 1998). Leaching totals decrease with increasing atomic number in the lanthanide series, to as little as 25 percent for Lu in the Illinois #6 sample.

Of the four leaching steps, leaching with HCl and with HNO_3 are the most effective in removing the REE. The sum of the HCl and HNO_3 leaching fractions shows a distinct decrease with increasing atomic number, but the trend for the Gascoigne-Wood #2 is less pronounced than that for the other two coals (Fig. 10b).

Data for the HCl and HNO_3 fractions are shown separately in Figure 10c. The figure shows the falloff in HNO_3 leaching percentages with atomic number to be less pronounced for the Gascoigne-Wood #2 than for the other coals, and that REE leaching fractions removed by HCL actually INCREASE in going from light to middle REE. This increase may be due to leaching of apatite, which is known to concentrate middle REE relative to heavy and light REE, on a normalized basis. Apatite was observed in the Gascoigne-Wood #2 sample by SEM-EDX.

Sums of HCl and HNO_3 leaching data are again plotted vs. atomic number in Figure 10d. Overall, the data show a gradual increase in organic association of the REE (indicated by the decreasing sums) with increasing atomic number. Querol and Huerta (1998) show a similar pattern for the Illinois #6 sample, but their results for the other two coals are less definitive. In the mineral fractions, our results indicate a predominance of LREE-enriched phases such as monazite vs. other REE-bearing phases. The Illinois #6 sample has the greatest organic association, especially for the HREE. Leaching patterns for the Wyee and Gascoigne-Wood #2 coals are similar for the LREE, but the Wyee shows a greater tendency towards organic association of the HREE.

Summary

Splits from three homogenized coal samples were analyzed by the USGS and other laboratories in an international interlaboratory comparison of coal chemistry, mineralogy, and elemental mode of occurrence. For bulk coal chemistry, the USGS uses a multi-technique approach that includes ICP-AES, ICP-MS, INAA, and element specific techniques for Hg and Se. Results obtained by this approach are internally consistent (based on leaching results) and generally in good agreement with those obtained by other labs. The poorest results, expressed as the percentage of variation for a given coal, were found for Hg, Cd, and Zn. Data for Hg and Cd reflect problems associated with determining sub-ppm concentrations of these elements.

Mode of occurrence information presented here for 35 elements and the REE is based primarily on selective leaching data, and integration of results obtained by SEM/EDX and XRD (to determine mineralogy), and electron microprobe analysis. For most elements, modes of occurrence determined by the USGS are similar to those found by other laboratories using differing approaches. Where there are differences between laboratories, these are primarily in the relative importance of specific modes. For example, our results suggest that Be occurs primarily in the silicate fraction (50-80%) with a 15-40 percent portion in the organic fraction, whereas Querol and Huerta (1998), using density separations, found Be to be primarily associated with organics. Likewise, for Se, our results indicate the fraction of pyrite-hosted Se in the Gascoigne-Wood #2 coal to be nearly 50 percent, whereas Huggins (1998) using XAFS considers this fraction to be minor, and

Querol and Huerta (1998) using analysis of density fractions find that nearly all of the Se is in pyrite (Table 2).

Interpretation of the selective leaching data is generally straightforward, but some discrepancies were found. For example, significant HNO_3-leachable fractions were found for Rb and Cs. Based on geochemical considerations these elements are expected to be not present in pyrite, and the mode of occurrence of the HNO_3-leachable fraction is unclear. Likewise, leaching data for Zn and Cd show unexpectedly large fractions of these elements leached by HNO_3. Electron microprobe analysis of Zn in pyrite fails to confirm the concentrations of Zn in pyrite indicated by the leaching data. For other elements, (e.g. Ni, As, and Cu) microprobe data for pyrite are consistent with average concentrations in pyrite indicated by leaching results. The combination of selective leaching, microanalysis, SEM/EDX and XRD provides mode of occurrence information on a large range of elements.

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Figure 1 - Lithium (A); Beryllium (B); Aluminum (C)

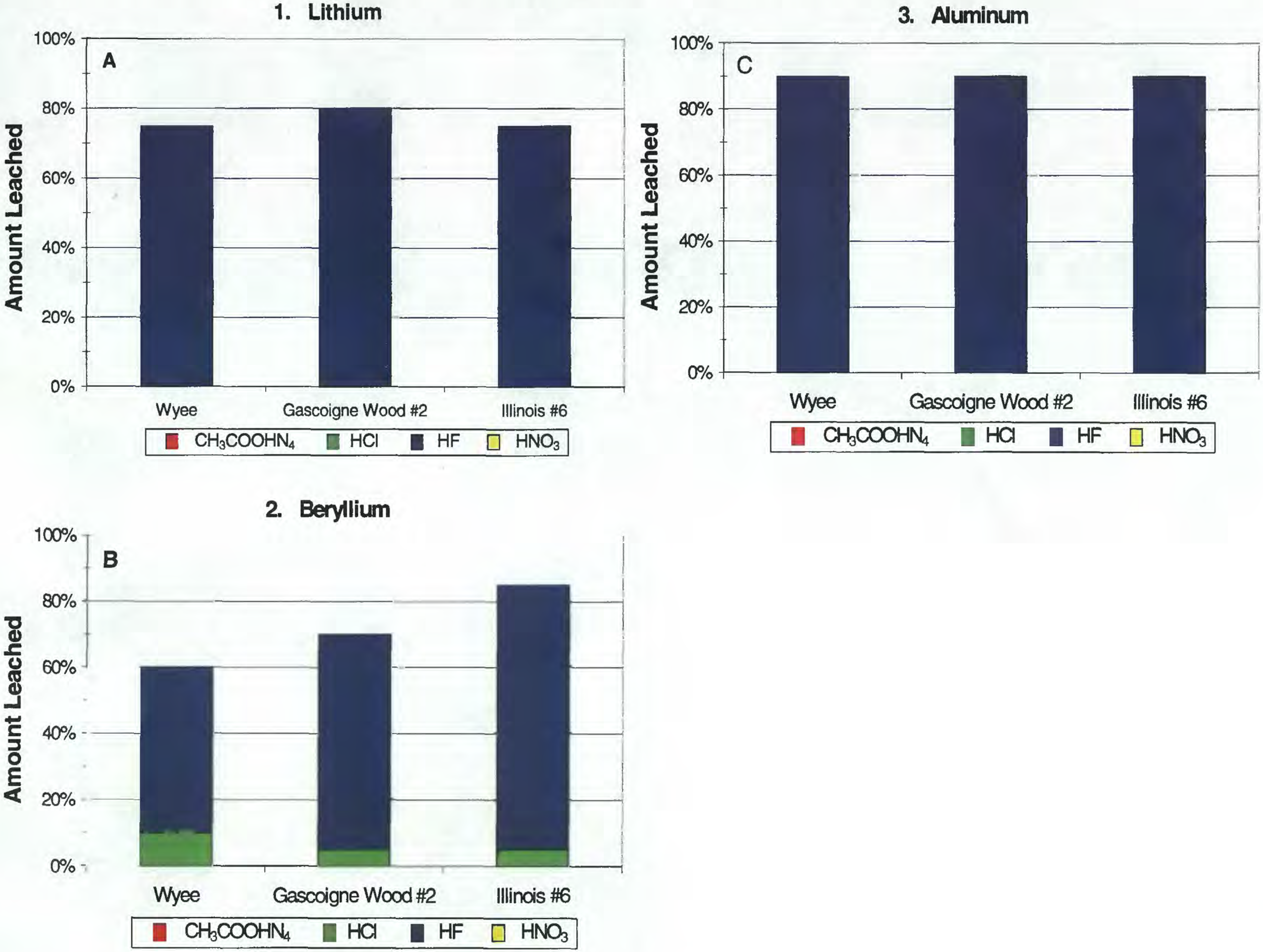


Figure 2 - Sodium (A); Potassium (B); Rubidium (C); Cesium (D)

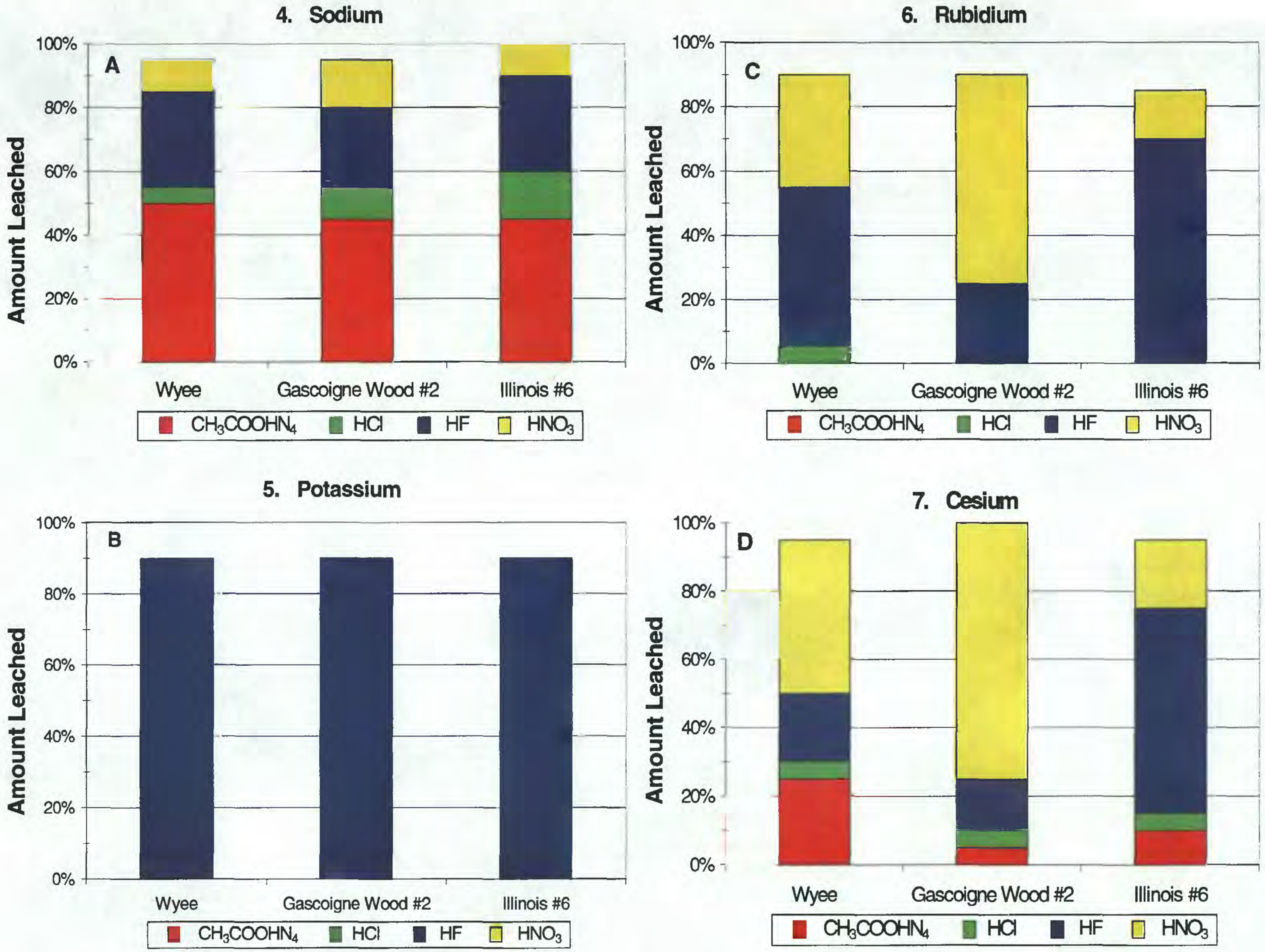


Figure 3 - Magnesium (A); Calcium (B); Strontium (C); Barium (D)

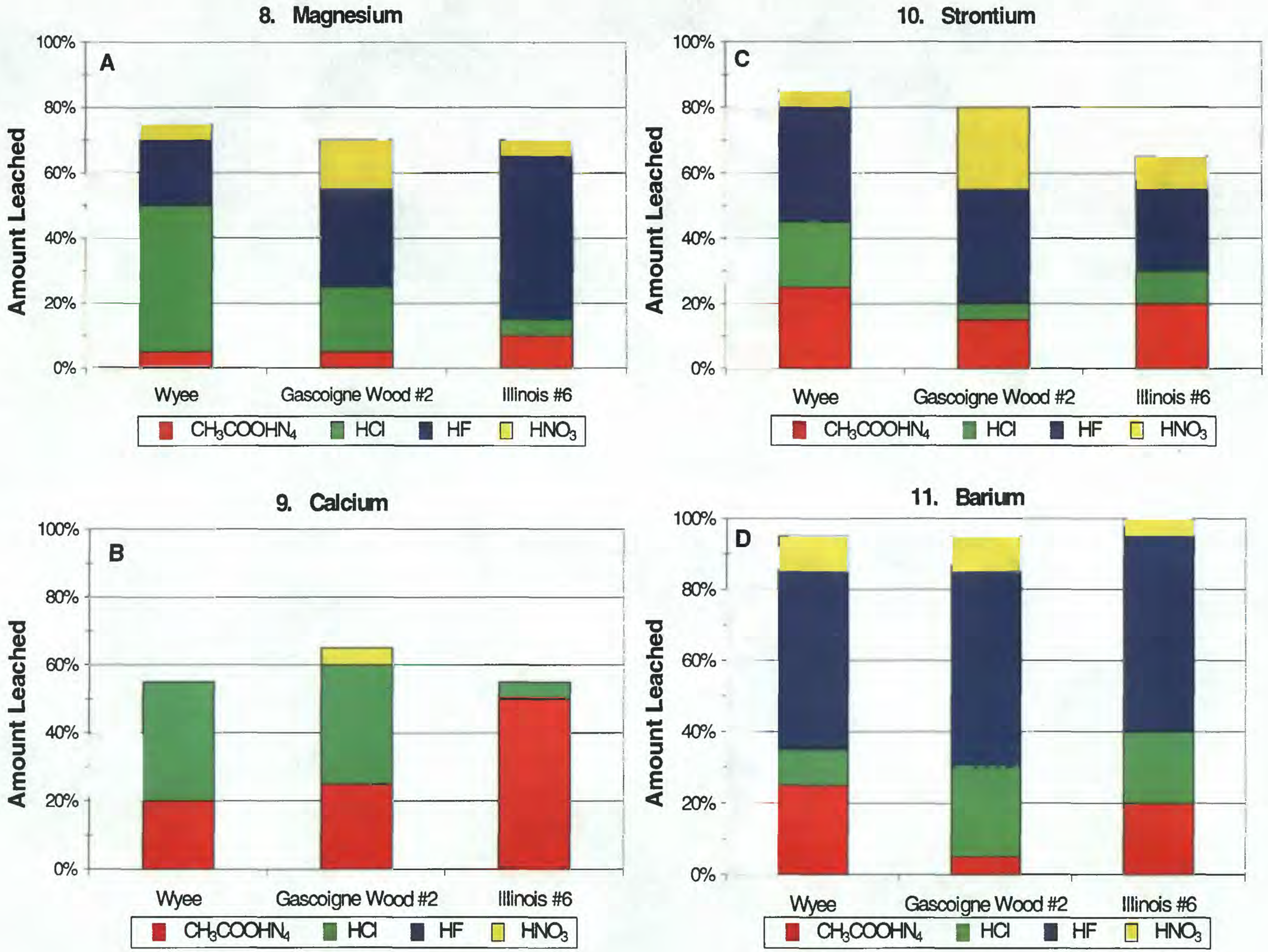


Figure 4 - Scandium (A); Titanium (B); Vanadium (C); Chromium (D)

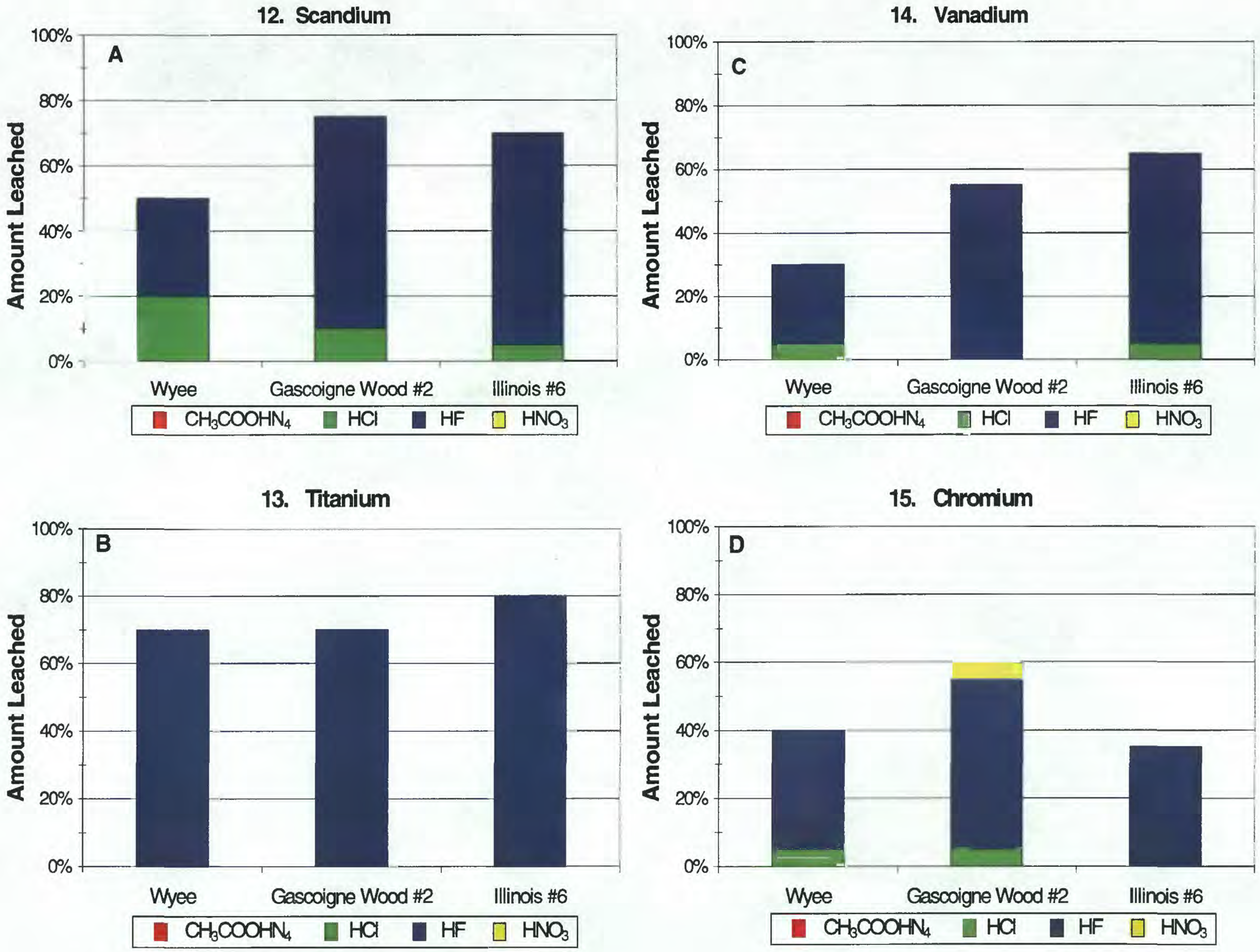


Figure 5 - Manganese (A); Iron (B); Cobalt (C); Nickel (D)

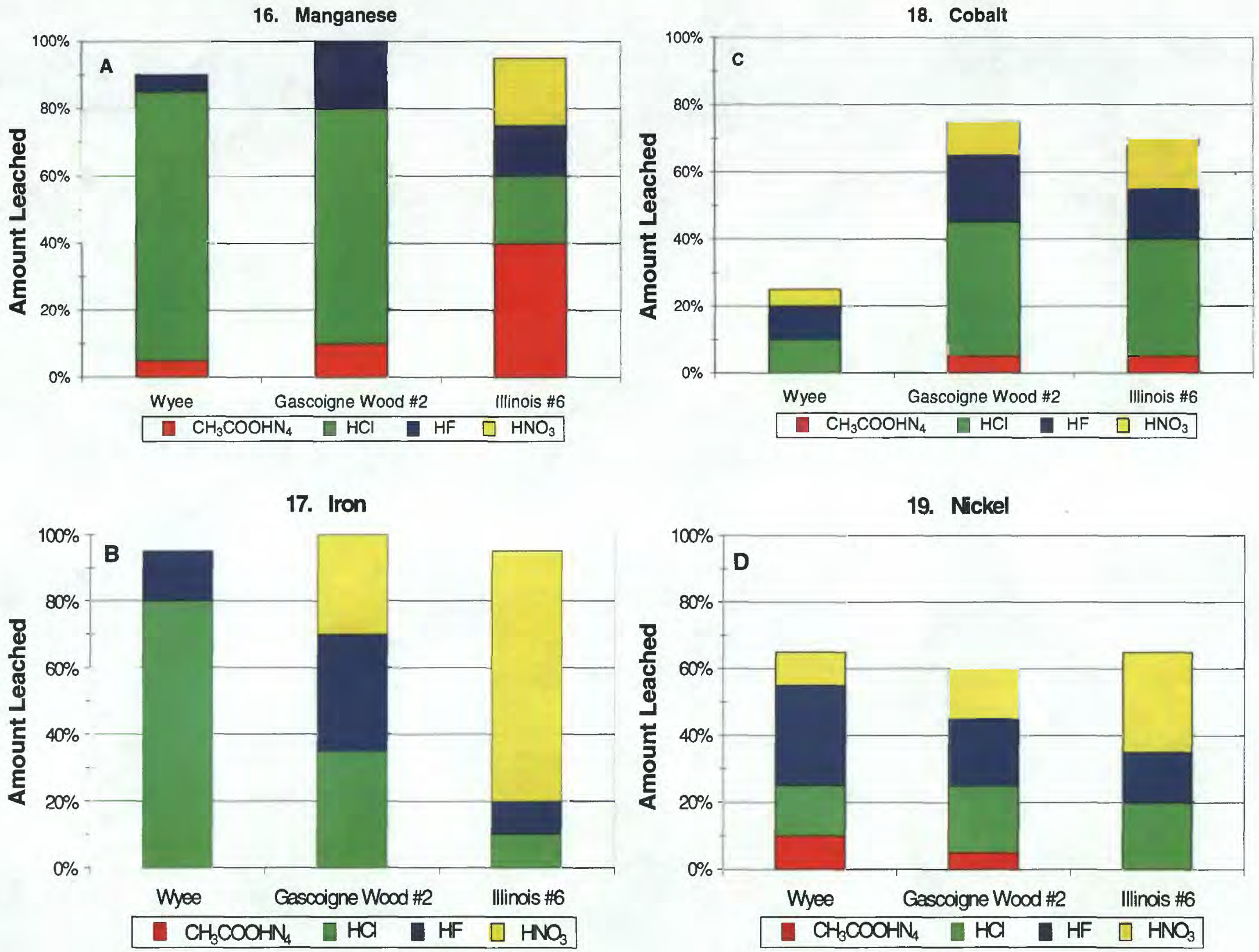


Figure 6 - Copper (A); Zinc (B); Molybdenum (C); Cadmium (D)

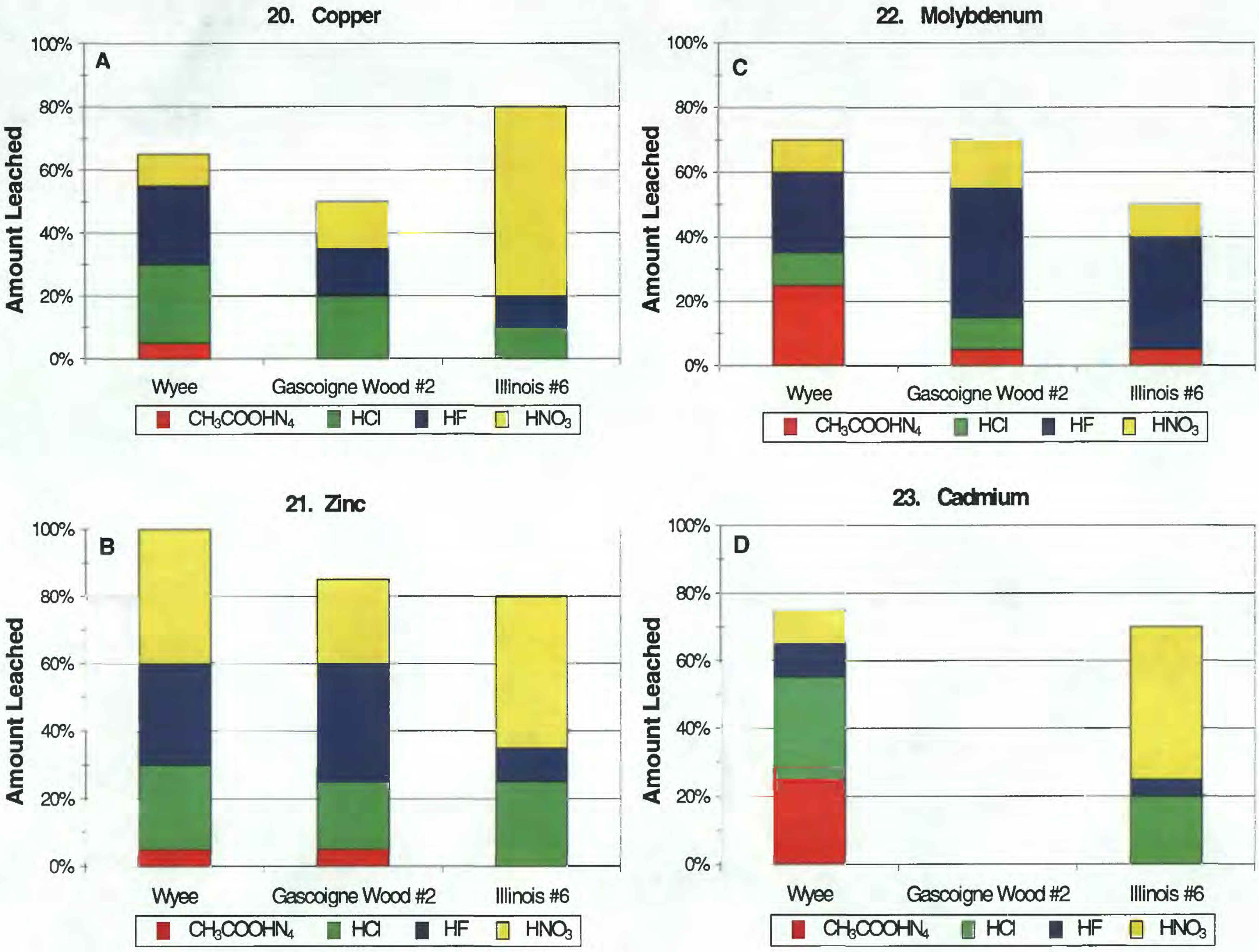
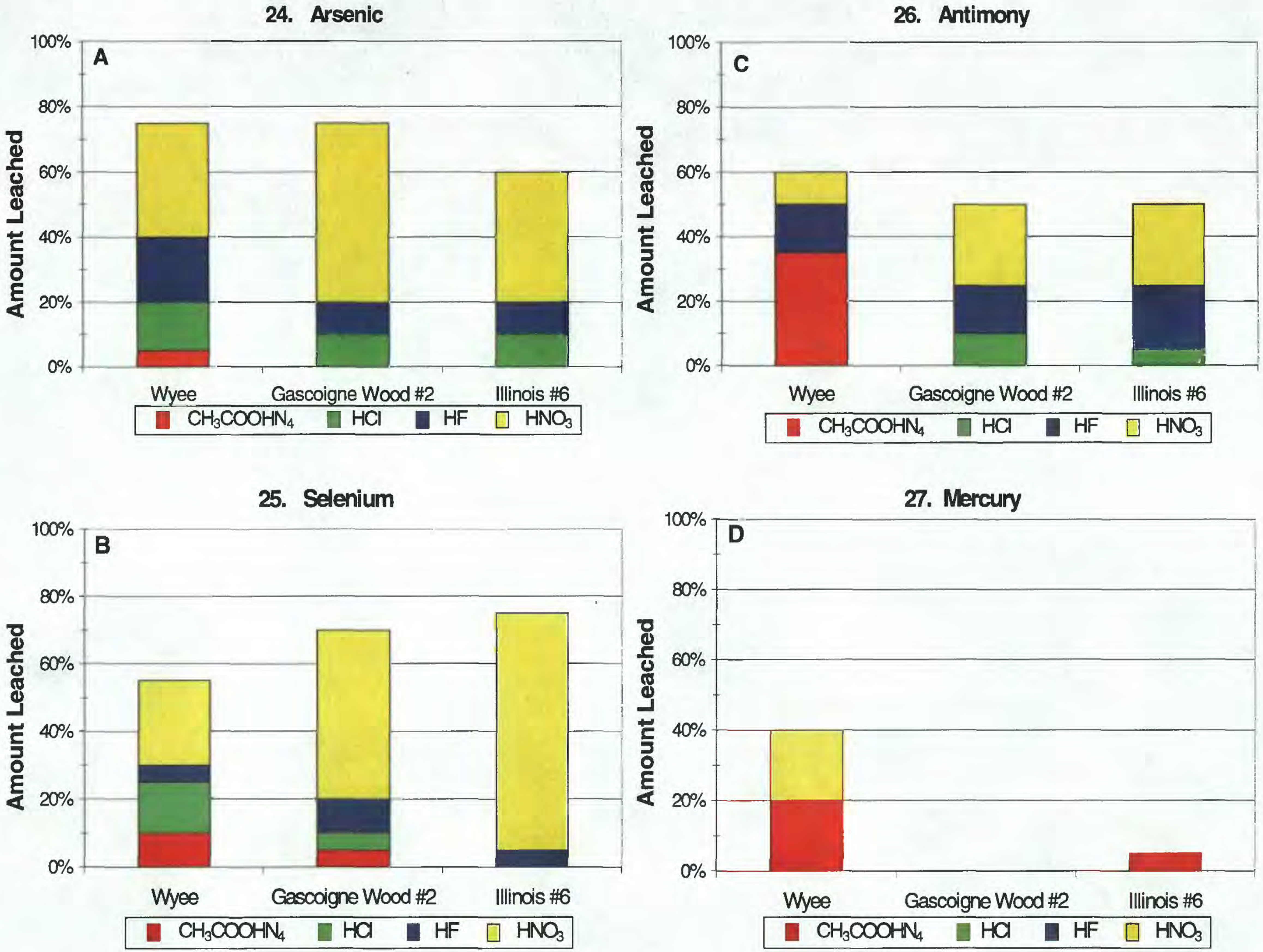


Figure 7 - Arsenic (A); Selenium (B); Antimony (C); Mercury (D)



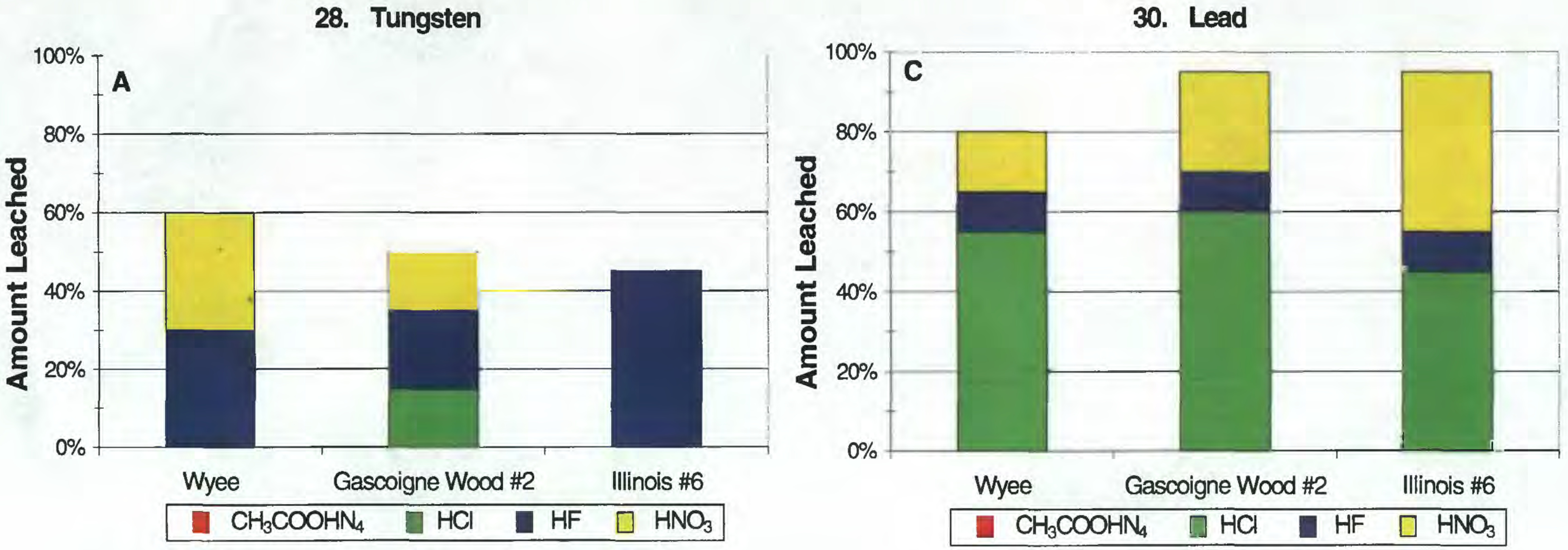
24. Arsenic

26. Antimony

25. Selenium

27. Mercury

Figure 8 - Tungsten (A); Thallium (B); Lead (C)


28. Tungsten

30. Lead

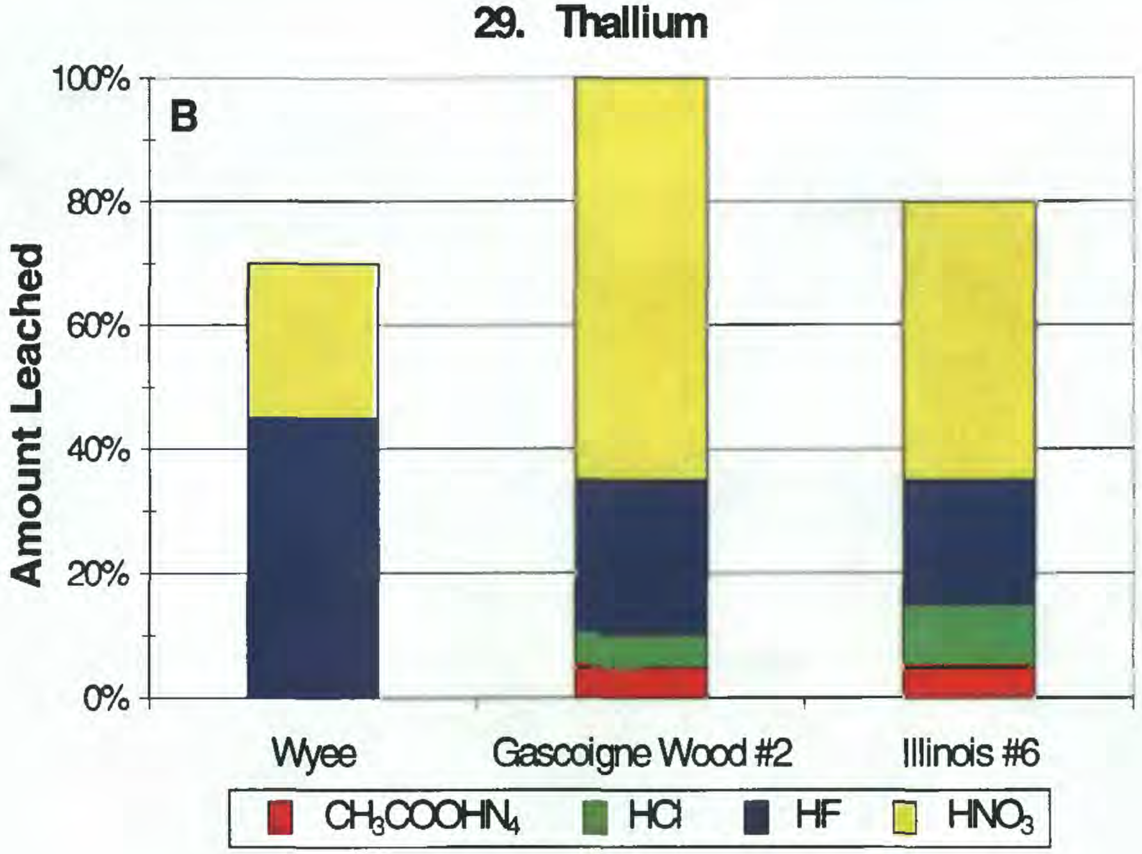
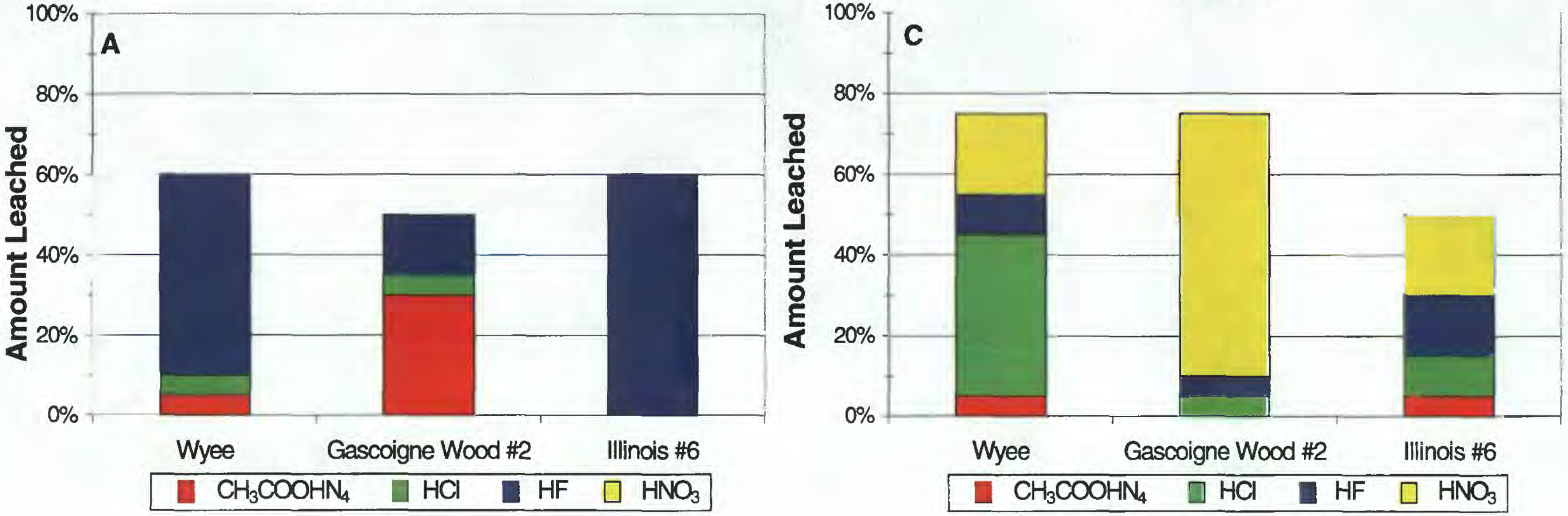

29. Thallium

Figure 9 - Hafnium (A); Tantalum (B); Thorium (C); Uranium (D)

31. Hafnium

33. Thorium



32. Tantalum

34. Uranium

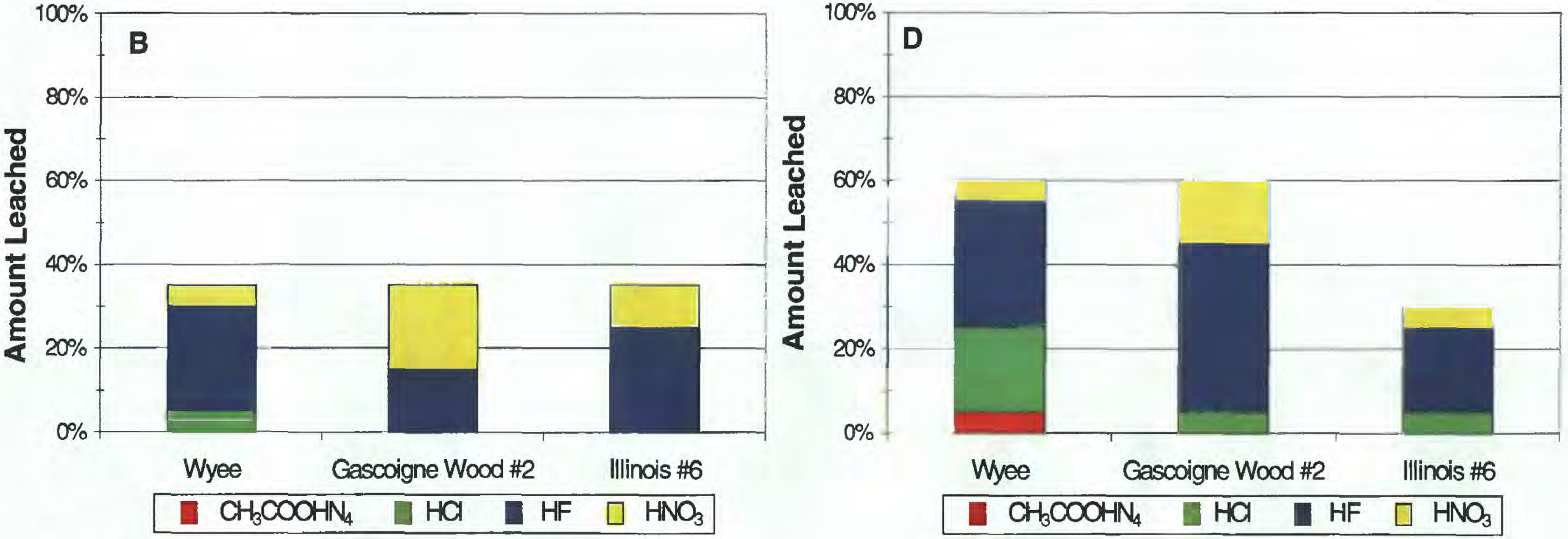
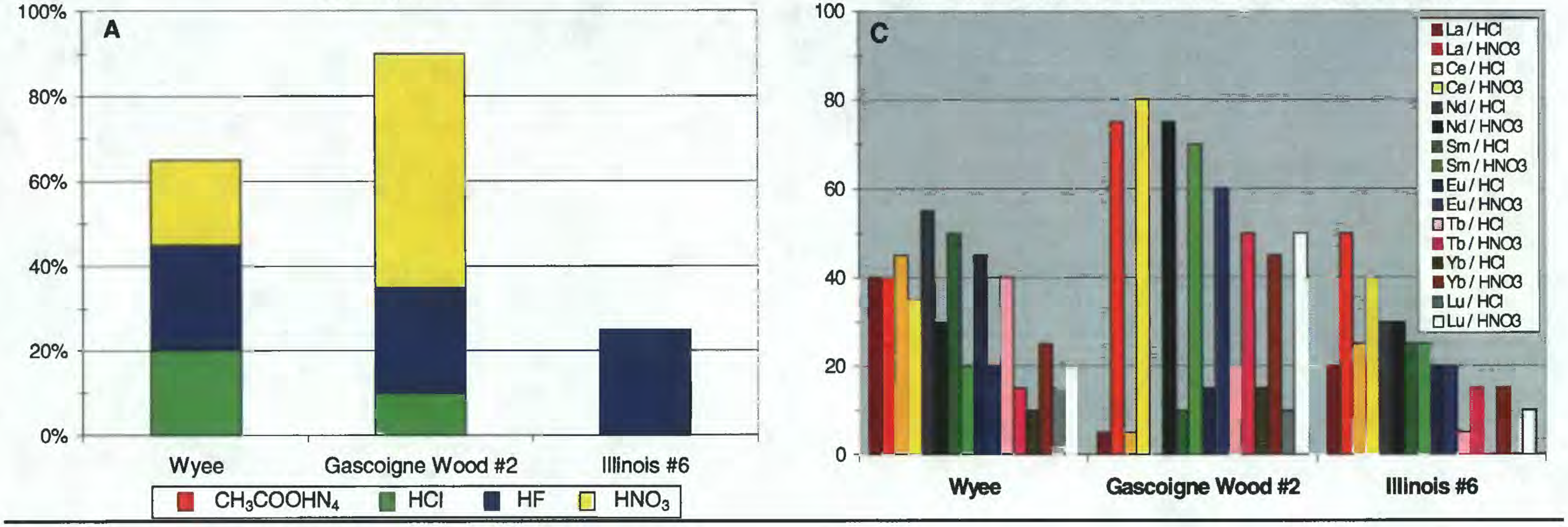


Figure 10 - Yttrium (A) and Rare Earth Elements (B-D)

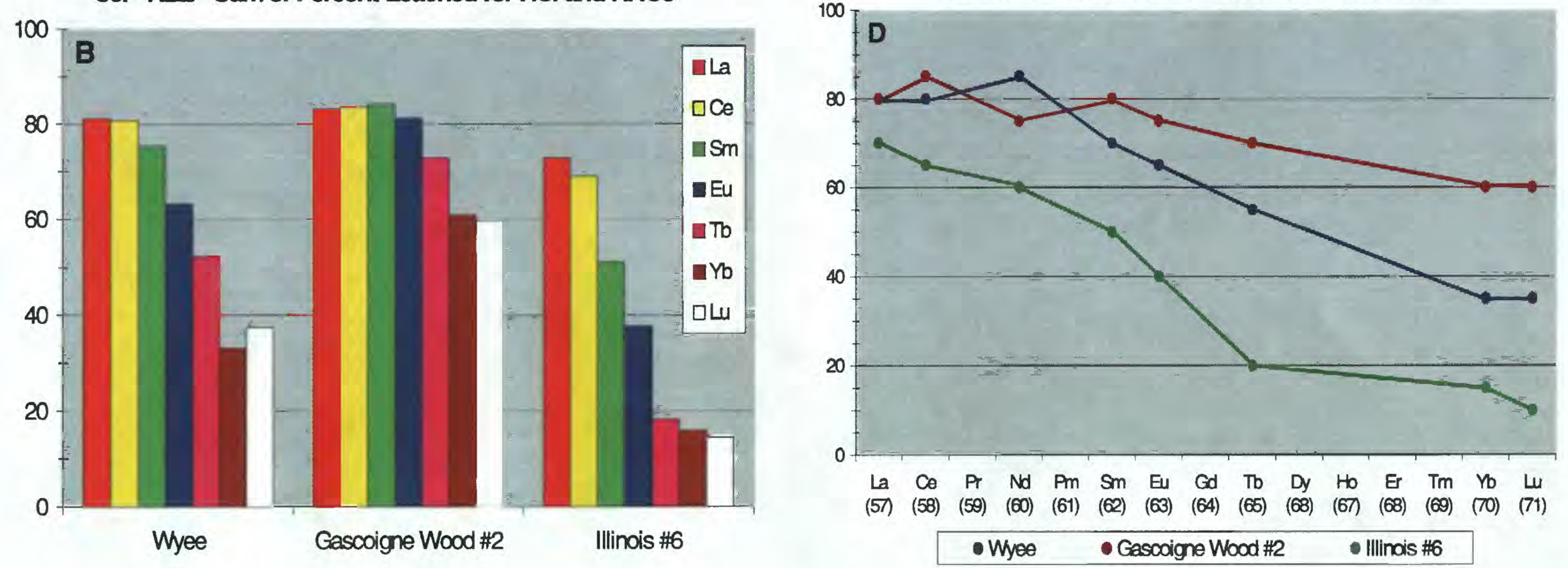
35. Yttrium

36. REE - Percent Leached For All Three Coals



36. REE - Sum of Percent Leached for HCl and HNO3

36. Sums of the percent leached by the HCl & HNO3 steps



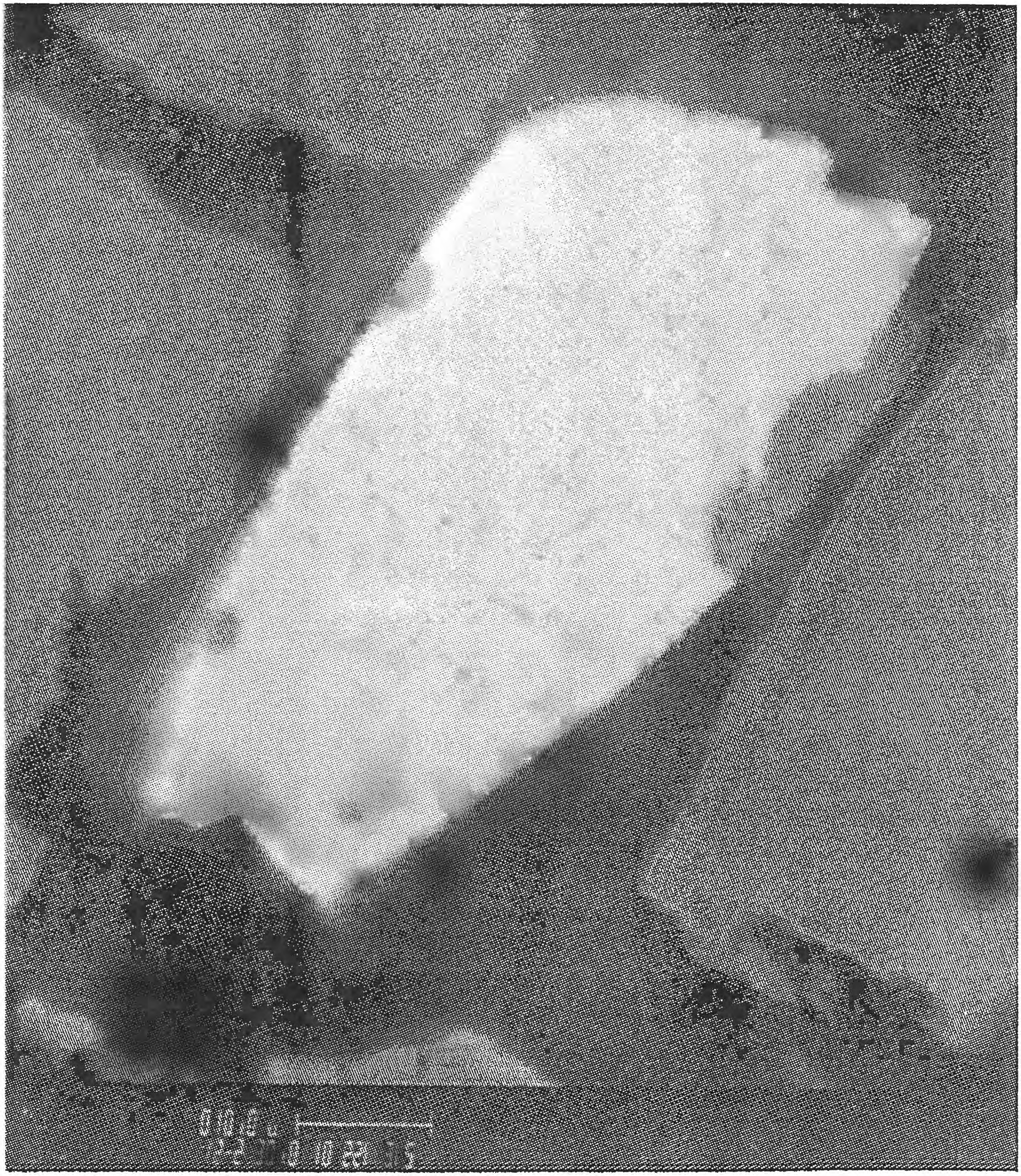


Figure 11. SEM photomicrograph showing circular areas of gorceixite ($BaAl_3(PO4)_2(OH)_5 \bullet H_2O$) at the margin of a large sphalerite grain (at the center of field of view) in the Wyee sample. Scale bar is 10 micrometers.

Appendix 1A. - Comparison of Chemical data for Wyee Coal determined by different labortories

Bulk Chemistry	Major elements reported in wt. % on an ash basis						
Technique	Combined Techniques			ICP only	ICPMS only	Spark MS	PIXE
Element	USGS*	A	B	C	D	E	F
Al_2O_3	21	21.42	22.1	21.8			18.4
CaO	4.1	3.69	3.66	5.8			2.93
Fe_2O_3	7.1	6.81	6.56	10.1			4.53
K_2O	2.6	2.69	2.35	2.4			2.12
MgO	1.5	1.83	1.37	1.7			.8
Na_2O	.86	.74	.82	1			
Si_2O	62			52.8			43.5
TiO_2	.89	.84	.86	1.7			.79

Trace elements reported in ppm on a whole-coal basis

Element	USGS*	A	B	C	D	E	F
As	3.0	2.1			2.53	2.8	
B	43	35	48				
Ba	149	140	139	138	136		
Be	1.4	1.3	.9	1.04		1.1	
Cd	.42	< .2	< .2		.52	.17	
Co	1.9	4	1.5		1.55	2	
Cr	10	7	<12.0	10.7	5.55	8	
Cs	2.3	2.1			1.87		
Cu	13.98	12	11	9.48	11.3	12	10
Ga	7.11	6.5	6.2		6.63		8
Ge	1.14		1.7		1		
Hg	.05	.07	.01			.04	.04
Li	11.4	12	6				
Mn	260	254	252			242	133
Mo	1.5	**<u>≤1.0</u>**	1.2		1.33	1.4	
Nb	4.7		3.5		3.87		
Ni	3.6	4	2			3	3
Pb	13.04	16	11		14.2	11.9	7
Rb	25	24			20.5		
Sb	1.1	.68	.8				
Sc	3.8	3.8		3.3			
Se	< .50	.5	<2.0			.68	
Sn	2.37		2				
Sr	104	73	100	94.8	84.45		87
Th	6.16	6.6	7.8		6.99		
Tl	.47		.4		.54		
U	1.9	1.9	1.7		2.29		
V	19.9	19	11.0	15.4	16.2		
Y	12.3			11.9	10.36		
Zn	15.1	37	6	16.6	20.29	19	11

Notes:

* - Ash value for the Wyee Coal is 23.70%

A - (Oxides) LTA values were used by converting to percent by weight using the ash value determined by USGS

B - (Oxides) Bulk coal values were converted to percent by weight using their lab's ash value 23.10%

C - (Elements) Values were converted from ppm in the ash to a bulk coal basis using USGS ash values

D - Values are based on average of two values; Ash value 23.48 %

E - Ash value 25.9 %

F - Ash value 23.1 %

KEY
(See text for discription of techniques)

ICP	ICP-MS	SparkMS
CVAA	AFS	Hydride Gen
INAA	PIXE	GFAA
	<u>AA</u>	

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Appendix 1B. - Comparison of Chemical data for Gascoigne Wood #2 coal determined by different labortories

Major elements reported in wt. % on an ash basis

Bulk Chemistry Technique	Combined Techniques			ICP only	ICPMS only	Spark MS	PIXE
Element	USGS*	A	B	C	D	E	F
Al_2O_3	24	25.2	26.1	24			21.9
CaO	2.6	2.29	2.71	2.7			1.68
Fe_2O_3	8.2	7.96	7.53	9.6			5.73
K_2O	3.4	3.74	3.40	4.3			3.28
MgO	1.9	1.48	1.78	1.7			.87
Na_2O	1.7	1.45	1.86	.7			
Si_2O	53			48.3			37.5
TiO_2	.98	.95	1.042	1.6			.86

Trace elements reported in ppm on a whole-coal basis

Element	USGS*	A	B	C	D	E	F
As	8.8	8.7			8.4	9	5.0
B	33.2	33	155				
Ba	237	247	274	246	235		
Be	1.7	1.7	1.3	1.5		1.5	
Cd	< .13	< .20	< .20			.082	
Co	5.8	8	6	5.1	5.5	6	
Cr	34.8	23	28	25.8	22.3		15.0
Cs	2.4	1.88			.95		
Cu	30.0	31	24	25	26.0	28	22
Ga	5.7	6.6	5.8		5.6		5
Ge	4.9		5.3		4.5		2.5
Hg	.03	.07	.06			.06	.07
Li	36.3	35	33				
Mn	110	108	119			108	70
Mo	3	**2**	2.9		2.85	2.9	
Nb	3.2		3.5		3.05		
Ni	19	18	16	17.5		18.1	14
Pb	12	14	10		12.5	12	9
Rb	25.6	25.3			16.4		
Sb	1.8	1.52	1.4				
Sc	4.6	4.57		4.3			
Se	.87	.9	<2.0			1.7	
Sn	<1.6		<1.0				
Sr	53.7	36	57	55.1	42.7		49
Th	2.8	3	3.6		2.5		
Tl	.32		.4		.4		
U	1.1	1.3	1		1.2		
V	47.4	40	42.0	38.9	40		36.0
Y	5.5			7.1	2.2		
Zn	19.7	39	19	22.1	21.4	22	12

Notes:

* - Ash value for the Gascoigne Wood #2 is 15.80 %;

A - (Oxides) Bulk coal values were converted to percent by weight using their lab's ash value 15.93%

B- (Oxides) Bulk coal values were used by converting to percent weight using ash value determined by USGS

C - (Elements) Values are based on average of two values except for Li and B (single value) and converted from ppm in the ash to a whole coal basis using USGS ash values

D- Values are based on average of two values; Ash Value 16.01 %

E - Ash value 17.5 %

F - Ash value 15.3 %

KEY
(See text for discription of techniques)

ICP	ICP-MS	SparkMS
CVAA	AFS	HGAA
INAA	PIXE	GFAA
	AA	

Appendix 1C. - Comparison of Chemical data for Illinois #6 Coal determined by different labortories

Bulk Chemistry — Major elements reported in wt. % on an ash basis

Technique	Combined Techniques			ICP only	ICPMS only	Spark MS	PIXE
Element	USGS*	A	B	C	D	E	F
Al_2O_3	17	19.41	18.189	17.9			17.1
CaO	4.5	4.54	4.2352	3.4			2.83
Fe_2O_3	21	19.37	17.851	8.9			11.37
K_2O	1.7	1.85	1.89	2.2			1.79
MgO	.87	1.12	.82	0.8			1.152
Na_2O	.6	.52	.93	0.8			
Si_2O	48			41.4			36.8
TiO_2	.96	1.12	.82	2			.85

Trace elements reported in ppm on a whole-coal basis

Element	USGS*	A	B	C	D	E	F
As	2.9	2	9		2.85	3.2	
B	229		352				
Ba	41.6		46	41.6	42.3		
Be	1.4		1	1.10		1.2	
Cd	.24	.4	.6			.27	
Co	3.4		3.2	2.6	.31	3.9	
Cr	23.9	17	23	18.7	16.1	23	17.0
Cs	0.98	1.1			.98		
Cu	8.7	8	8	6.76	8.28	9	5
Ga	3.4		2.9		3.25		4
Ge	5.2		4.7		4.6		4.0
Hg	.05	.08	0.1			.07	.09
Li	9.6	9	11				
Mn	36.4	37	40			35	18
Mo	6.6	4	5.3		5.41	6.1	
Nb	3.1		2.2		2.18		
Ni	12.5	12	11	11.4		13	8
Pb	13.5	14	11		13.4	12	7
Rb	14.5	12			12.1		
Sb	.41	.34	.4				
Sc	2.5	2.4		2.08			
Se	2.2	1.9	<2.0			2.5	
Sn	<1.0		<1.0				
Sr	28.1	20	26	25.5	23.7		30
Th	2.2	1.7	2.1		2		
Tl	0.69		0.5		0.67		
U	1.3	1.6	1.4		1.81		
V	27	24	33.0	22.88	23.9		
Y	5.4			5.2	2.45		
Zn	71	103	86	70.2	69.8	63	27

Notes:

* - Ash value for the Illinois #6 is 10.40 %

A - (Oxides) Bulk coal values were converted to percent by weight using their lab's ash value 10.17%

B - (Elements) Values were converted from ppm in the ash to a bulk coal basis using USGS ash values

C - Ash value 12.6 %

D - Ash value 10.1 %

E - (Oxides) LTA values were used by converting to percent by weight using the ash value determined by USGS

F - Values are based on average of two values; Ash value 10.31

KEY

(See text for discription of techniques)

ICP	ICP-MS	SparkMS
CVAA	AFS	Hydride Gen
INAA	PIXE	GFAA
	AA	

Appendix 2. Comparison of Ash and Chemical data. Data on whole coal basis, in ppm except as noted.

	Wyee Coal	Gascoigne Wood # 2	Illinois #6
Ash (%)	23.7	15.8	10.4
Li	11.4	36.3	9.6
Be	1.4	1.7	1.4
Al (%)	2.6	2.0	.94
Na	1500	2000	500
K	5100	4500	1500
Rb	25	25.6	14.5
Cs	2.3	2.4	.98
Mg	2100	1800	550
Ca	7000	2900	3300
Sr	104	53.7	28.1
Ba	149	237	41.6
Sc	3.8	4.6	2.5
Ti	1300	930	600
V	19.9	47.4	27
Cr	10	34.8	23.9
Mn	260	110	36.4
Fe (%)	1.2	.91	1.5
Co	1.9	5.8	3.4
Ni	3.6	19	12.5
Cu	14	30.0	8.7
Zn	15.1	19.7	71
Mo	1.5	3	6.6
Cd	.42	< .13	.24
As	3.0	8.8	2.9
Se	< .5	.87	2.2
Sb	1.1	1.8	.41
Hg	.05	.03	.05
W	2.04	.69	.36
Tl	.47	.32	.69
Pb	13	12	13.5
Hf	2.4	2.3	.48
Ta	.35	.23	.14
Th	6.2	2.8	2.2
U	1.9	1.1	1.3
La	13.9	11.9	4.8
Ce	25.3	19.7	8.9
Nd	9	7.6	3.3
Sm	2.8	2.1	.98
Eu	.44	.4	.2
Tb	.37	.22	.13
Yb	1.3	.84	.52
Lu	.19	.12	.067
Y	12.3	5.5	5.4
B	43	33.2	229
Si (%)	6.9	3.9	2.3
Ga	7.1	5.7	3.4
Ge	1.1	4.9	5.2
Nb	4.7	3.2	3.1

Appendix 3. Low Temperature Ash Yield and Mineralogy by XRD.

(Values in parenthesis on a whole coal basis. All values in percent.)

Mineral	Wyee	Gascoigne Wood #2	Illinois #6
	LTA	LTA	LTA
Quartz	30(7.7)	20(3.4)	25(3.4)
Feldspars	10(2.6)	< 1(<.2)	< 1(<.2)
Carbonates	< 5(<1.3)	<5(<1)	5(0.7)
Illite	20(5.1)	35(6.0)	10(1.3)
Kaolinite	35(9.0)	30(5.1)	45(6.0)
Chlorite	ND	10(1.7)	ND
Pyrite	ND	< 5(<1)	15(3.0)
% LTA Ash	25.6	17.1	13.4

ND = Not detected

Appendix 4. Minor and trace phase mineralogy (SEM)

Coal Sample	Minerals
Wyee	
	Monazite (rare earth phosphate)
	Ilmenite
	Pyrite
	Uraninite
	Chalcopyrite
	Galena
	Gypsum
	Barite
	Crandallite Group (Sr)
	Rutile
	Mo, Pb, Cu, Sb Sulfide
	Chromite
	Argentite
	Lead Selenide
	Cassiterite
Gascoigne Wood #2	
	Pyrite
	Gypsum
	Barite
	Rutile
	Sphalerite (Cd)
	Zircon (Hf)
	Amphibole
	Fe, Ni, Cu Sulfide
	Lead Selenide (in Pyrite)
	Galena
	Apatite
Illinois #6	
	Pyrite
	Sphalerite (Cd)
	Fe Oxide
	Chromite
	Barite

Mineral identification by SEM is based on morphology and elemental composition of grains determied with an energy dispersive x-ray analytical system (EDX)

Appendix 5. Microprobe Analyses, Pyrite in Gascoigne-Wood #2 sample

Analysis Number	Se	Cu	Ni	As	Zn	Cd	Co*	Fe	S	Total	Sample Reference	Size and Form (micrometers)
10	< .01	< .01	< .01	.10	< .01	< .01	< .01	47.40	49.40	96.95	(A)Py1.1	70 x 120 subhedral
11	< .01	< .01	< .01	.12	< .01	< .01	.02	47.40	49.57	97.17	(A)Py1.2	
12	< .01	< .01	< .01	.12	< .01	< .01	.01	46.99	49.94	97.10	(A)Py1.3	
13	< .01	< .01	< .01	.10	.01	< .01	.02	47.53	50.33	98.04	(A)Py1.4	
14	< .01	.02	< .01	.49	.01	< .01	.01	47.00	51.22	98.80	(A)Py2.1	75 x 90 composite subhedral
15	.02	< .01	< .01	.35	.01	< .01	.01	48.01	52.41	100.85	(A)Py2.2	
16	< .01	< .01	< .01	.26	.01	< .01	.02	47.92	51.71	99.96	(A)Py2.3	
17	< .01	.01	< .01	.35	< .01	< .01	.01	47.44	51.01	98.88	(A)Py2.4	
18	< .01	.03	< .01	.08	.01	< .01	.02	47.51	53.58	101.27	(A)Py3.1	50 x 120 subhedral
19	< .01	< .01	< .01	.07	< .01	< .01	.02	47.12	53.46	100.73	(A)Py3.2	
20	< .01	.02	.00	.50	.03	< .01	.01	48.25	52.54	101.40	(A)Py4.1	60 x70 subhedral wi. euhedral overgr.
21	< .01	.01	.01	.07	< .01	< .01	< .01	48.20	52.64	100.99	(A)Py4.2	
22	< .01	.02	.04	.30	< .01	< .01	.01	48.65	45.63	94.70	(A)Py4.3	
23	< .01	.01	.05	.06	< .01	< .01	.02	46.90	52.38	99.45	(A)Py4.4	
24	< .01	.04	.08	.16	.02	< .01	.01	47.68	50.83	98.87	(A)Py5.1	60 x 60 subhedral
25	.02	.04	.12	.19	.03	< .01	.02	47.42	50.99	98.88	(A)Py5.2	
26	.02	.04	.15	.30	< .01	< .01	.02	47.38	51.90	99.86	(A)Py5.3	
27	.01	.04	.09	.19	.04	< .01	.03	47.30	51.52	99.25	(A)Py5.4	
29	< .01	< .01	< .01	.17	.01	< .01	.01	47.69	49.31	97.24	(A)Py6.2	75 x 80 subhedral
30	< .01	< .01	< .01	.15	< .01	< .01	.01	47.67	52.79	100.67	(A)Py6.3	
33	.01	.04	< .01	.25	< .01	< .01	.02	46.61	51.15	98.12	(A)Py8.1	60 x 100 composite subhedral
34	< .01	.03	< .01	.23	< .01	< .01	< .01	46.72	51.13	98.16	(A)Py8.2	
35	< .01	.02	< .01	.22	< .01	< .01	< .01	47.02	51.14	98.45	(A)Py8.3	
36	< .01	.01	< .01	.01	.01	< .01	.01	47.88	52.66	100.62	(A)Py9.1	50 x 60 composite subhedral
37	.04	< .01	< .01	.09	< .01	< .01	.01	45.47	49.13	94.79	(A)Py9.2	
38	< .01	.00	< .01	.19	.01	< .01	< .01	46.85	51.23	98.33	(A)Py9.3	
39	.01	.02	.03	.01	.01	< .01	.01	47.13	47.01	94.28	(A)Py10.1	30 framboid
42	< .01	.03	< .01	.40	< .01	< .01	< .01	47.26	50.63	98.37	(A)Py11.2	70 x 70 composite subhedral
43	< .01	.02	< .01	.83	< .01	< .01	.01	46.40	50.07	97.38	(A)Py11.3	

Appendix 5.-continued. Microprobe Analyses, Pyrite in Gascoigne-Wood #2 sample

No.	Se	Cu	Ni	As	Zn	Cd	Co**	Fe	S	Total	Reference	Size and Form (micrometers)
44	< .01	< .01	< .01	.21	.01	< .01	.01	47.81	52.70	100.79	(A)Py12.1	35 x 60 subhedral
45	< .01	.04	.00	.40	.01	< .01	.01	47.10	52.19	99.79	(A)Py12.1	
46	.01	< .01	.01	.02	< .01	< .01	.01	47.85	52.37	100.31	(A)Py13.1	15 framboid
47	< .01	.02	.05	.01	.01	< .01	< .01	48.22	52.22	100.58	(A)Py14.1	17 framboid
48	< .01	.03	< .01	.14	.01	< .01	.01	45.48	48.89	94.61	(D)Py1.1	70 x 100 composite subhedral
49	< .01	.06	.08	.22	.03	< .01	< .01	47.10	50.47	98.01	(D)Py1.2	
50	< .01	.01	.04	.12	.00	< .01	.01	47.31	51.00	98.54	(D)Py1.3	
51	< .01	.03	.00	.11	.01	< .01	< .01	46.59	50.26	97.06	(D)Py1.4	
53	< .01	< .01	.01	1.92	.01	< .01	.02	47.51	50.19	99.71	(D)Py2.2	55 x 65 subhedral
54	< .01	< .01	< .01	.88	< .01	< .01	< .01	48.00	51.06	99.99	(D)Py2.3	
55	< .01	.01	.01	.06	< .01	< .01	.01	48.55	51.98	100.67	(D)Py3.1	80 x 90 subhedral
56	< .01	< .01	.11	.13	.01	< .01	.02	48.28	50.91	99.50	(D)Py3.2	
57	< .01	.01	< .01	.69	.01	< .01	.02	48.23	51.44	100.43	(D)Py3.3	
58	< .01	< .01	< .01	.38	.02	< .01	< .01	48.69	51.84	100.99	(D)Py3.4	
59	< .01	< .01	.01	.30	< .01	< .01	< .01	48.43	50.53	99.31	(D)Py3.5	
60	< .01	< .01	< .01	.24	< .01	< .01	.01	48.29	51.53	100.12	(D)Py5.1	40 x 75 composite subhedral
61	< .01	< .01	< .01	.20	< .01	< .01	.01	48.01	51.88	100.16	(D)Py5.2	
62	< .01	.01	< .01	.10	< .01	< .01	< .01	48.46	52.97	101.59	(D)Py5.3	
63	< .01	< .01	.01	.01	.02	< .01	.01	48.99	51.55	100.65	(D)Py6.1	50 anhedral (round)
64	< .01	< .01	.01	.01	.02	< .01	.02	48.41	50.83	99.35	(D)Py6.2	
65	< .01	.01	.01	.01	.03	< .01	< .01	48.35	50.38	98.84	(D)Py6.3	
66	< .01	< .01	< .01	.35	.01	< .01	.01	47.56	51.44	99.42	(D)Py7.1	35 x 60 subhedral
67	< .01	< .01	.01	.27	< .01	< .01	.01	48.42	51.59	100.35	(D)Py7.2	
68	< .01	.01	< .01	.30	.03	< .01	< .01	48.20	50.73	99.31	(D)Py7.3	
70	< .01	.02	.03	.01	.01	< .01	.01	47.49	48.66	96.28	(D)Py8.2	20 framboid
71	< .01	.03	.04	.01	.02	< .01	.01	48.49	51.68	100.34	(D)Py9.1	40 x 40 subhedral
72	< .01	.03	.06	.01	.02	< .01	.01	48.33	50.85	99.37	(D)Py9.2	
73	< .01	.04	.03	.00	.01	< .01	.01	48.35	50.97	99.45	(D)Py9.3	

Appendix 5.-continued. Microprobe Analyses, Pyrite in Gascoigne-Wood #2 sample

No	Se	Cu	Ni	As	Zn	Cd	Co*	Fe	S	Total	Reference	Size and Form (micrometers)
77	<.01	.02	.03	<.01	.01	<.01	.01	48.88	51.32	100.32	(D)Py11.1	25 framboid
78	<.01	.07	.05	.01	.04	<.01	.01	47.95	51.46	99.62	(D)Py11.2	30 framboid
79	<.01	.10	.05	.02	.01	<.01	<.01	47.80	50.82	98.83	(D)Py11.3	
80	.01	.02	.21	.06	<.01	<.01	.03	47.06	49.74	97.18	(D)Py12.1	30 x 35 composite subhedral
81	<.01	.02	.19	.09	<.01	<.01	.02	47.49	50.30	98.15	(D)Py12.2	
82	.00	.01	<.01	.24	.02	<.01	.01	47.75	49.98	98.05	(D)Py13.1	25 x 45 subhedral
83	.03	.03	<.01	.21	<.01	<.01	.01	47.65	50.48	98.46	(D)Py13.2	
84	.02	.03	.07	.06	<.01	<.01	.01	48.60	50.31	99.15	(D)Py14.1	45 x 95 composite subhedral
85	.01	.04	.06	.10	.01	<.01	.01	48.55	50.66	99.48	(D)Py14.2	
86	.02	.03	.06	.08	<.01	<.01	.00	48.67	51.46	100.37	(D)Py14.3	

* ~0.05 wt. % contribution of Fe interference has been subtracted from Co values.

Appendix 5.-continued. Microprobe Analyses, Pyrite in Gascoigne-Wood #2 sample

Analysis Number	Se	Cu	Ni	As	Zn	Cd	Co*	Fe	S	Total	Sample Reference	Size and Form (micrometers)
88	< .01	.01	< .01	.01	0.01	< .01	0.00	48.26	50.27	98.60	(A)Py1.2	80 x 130 plumose
90	< .01	< .01	< .01	< .01	< .01	< .01	.01	46.63	48.29	94.98	(A)Py2.2	80 x 100 plumose
91	< .01	.01	< .01	< .01	.01	< .01	< .01	48.56	52.00	100.63	(A)Py4.1	50 x 60 composite subhedral
93	.01	< .01	< .01	.01	.01	< .01	< .01	48.30	51.04	99.42	(A)Py5.1	100 x 100 composite subhedral
94	< .01	< .01	< .01	.01	.01	< .01	< .01	48.68	51.51	100.25	(A)Py5.2	
95	.01	< .01	< .01	< .01	.01	< .01	< .01	48.45	52.14	100.66	(A)Py5.3	
96	< .01	< .01	< .01	< .01	.02	< .01	< .01	48.54	52.43	101.04	(A)Py5.4	
99	< .01	< .01	< .01	< .01	.02	< .01	< .01	47.39	46.64	94.11	(A)Py7.2	125 x 125 subhedral
100	< .01	< .01	.01	< .01	.01	< .01	< .01	47.86	53.59	101.52	(A)Py7.3	
101	< .01	< .01	< .01	< .01	< .01	< .01	< .01	48.72	53.77	102.54	(A)Py7.4	
102	.01	.02	< .01	< .01	< .01	< .01	.01	47.47	52.16	99.73	(A)Py8.1	70 x 80 composite subhedral
103	< .01	.04	< .01	< .01	< .01	< .01	< .01	47.32	52.07	99.48	(A)Py8.2	
104	< .01	.01	.02	.04	.01	< .01	.02	47.25	51.92	99.31	(A)Py8.3	
105	< .01	.01	< .01	.01	< .01	< .01	.01	48.41	52.16	100.64	(A)Py9.1	70 x 130 subhedral
106	.01	< .01	< .01	.01	< .01	< .01	< .01	48.64	52.28	100.99	(A)Py9.2	
107	< .01	< .01	< .01	< .01	< .01	< .01	< .01	48.63	52.51	101.19	(A)Py9.3	
108	< .01	.01	< .01	.01	.01	< .01	< .01	48.62	53.02	101.72	(A)Py9.4	
109	< .01	< .01	< .01	.01	.01	< .01	< .01	48.18	53.27	101.53	(A)Py9.5	
110	< .01	< .01	.01	< .01	.04	< .01	< .01	47.55	51.47	99.12	(A)Py10.1	40 framboid in cluster
111	< .01	.01	.01	< .01	.01	< .01	< .01	47.68	51.59	99.34	(A)Py10.2	
112	< .01	< .01	< .01	< .01	< .01	< .01	< .01	47.92	52.52	100.49	(A)Py10.3	
113	.01	< .01	< .01	< .01	.02	< .01	< .01	47.82	52.89	100.79	(A)Py11.1	35 framboid
114	< .01	< .01	< .01	.01	< .01	< .01	< .01	47.16	52.09	99.30	(A)Py11.2	
115	.01	< .01	< .01	.01	.02	< .01	< .01	48.10	51.41	99.59	(A)Py12.1	35 x 45 composite subhedral
116	< .01	< .01	< .01	.01	.01	< .01	< .01	47.83	52.22	100.12	(A)Py12.2	
117	< .01	< .01	.03	< .01	.01	< .01	< .01	48.26	52.14	100.50	(A)Py13.1	30 framboid in cluster
118	.01	< .01	.02	< .01	< .01	< .01	.01	48.90	53.34	102.33	(A)Py13.2	

Appendix 5.-continued. Microprobe Analyses, Pyrite in Illinois #6 sample

No.	Se	Cu	Ni	As	Zn	Cd	Co*	Fe	S	Total	Reference	Size and Form (micrometers)
119	.01	< .01	< .01	< .01	.01	.00	< .01	48.30	51.80	100.18	(A)Py13.3	25 framboid in cluster
120	< .01	< .01	< .01	< .01	< .01	< .01	< .01	48.14	51.71	99.91	(A)Py13.4	
121	< .01	.02	< .01	.01	.01	< .01	< .01	47.86	51.84	99.78	(A)Py14.1	90 x 150 composite anhedral/subhedral
122	< .01	< .01	< .01	< .01	.01	< .01	< .01	48.52	52.74	101.33	(A)Py14.2	
123	< .01	.02	< .01	.01	.01	< .01	< .01	46.92	51.14	98.15	(A)Py14.3	
125	< .01	< .01	< .01	< .01	.01	< .01	< .01	48.02	53.25	101.32	(D)Py1.2	60 x 80 composite subhedral
126	< .01	< .01	< .01	< .01	.02	< .01	< .01	47.52	51.45	99.04	(D)Py1.3	
130	< .01	.05	.06	< .01	.01	< .01	< .01	46.97	50.84	97.98	(D)Py3.1	100 x 120 composite
131	< .01	.08	< .01	.02	.01	< .01	< .01	47.25	50.98	98.38	(D)Py3.2	
132	< .01	.07	.01	.01	.03	< .01	< .01	46.63	51.16	97.97	(D)Py3.3	
133	.01	.05	.01	.01	.01	< .01	< .01	46.39	51.53	98.05	(D)Py3.4	
134	.01	.01	< .01	< .01	.02	< .01	< .01	48.20	51.87	100.16	(D)Py4.1	20 x 50 subhedral (cleat?)
135	.01	< .01	< .01	.01	.01	< .01	.02	47.84	52.97	100.91	(D)Py4.2	
136	< .01	.01	< .01	< .01	.01	< .01	.01	48.66	51.75	100.48	(D)Py5.1	70 x 85 composite
137	< .01	< .01	< .01	.01	< .01	< .01	.00	48.18	52.95	101.19	(D)Py5.2	
138	< .01	< .01	< .01	.00	.02	< .01	.01	48.35	51.38	99.81	(D)Py5.3	
139	< .01	< .01	< .01	< .01	.01	< .01	< .01	47.25	50.31	97.63	(D)Py5.4	
140	< .01	< .01	.02	.03	.03	< .01	.01	47.93	50.07	98.14	(D)Py6.1	30 framboid in cluster
141	< .01	< .01	.03	.01	.02	< .01	.01	46.89	50.82	97.82	(D)Py6.2	
142	< .01	< .01	.01	.01	< .01	< .01	< .01	47.59	51.70	99.34	(D)Py6.3	15 framboid
144	< .01	< .01	< .01	.01	.02	< .01	< .01	47.61	48.81	96.50	(D)Py7.2	100 x 175 composite
146	< .01	< .01	< .01	.01	< .01	< .01	< .01	46.13	50.18	96.37	(D)Py8.1	55 x125 subhedral
147	.01	< .01	< .01	.01	.01	< .01	< .01	45.99	50.15	96.22	(D)Py8.2	
150	< .01	.02	.01	< .01	.02	< .01	< .01	43.73	50.21	94.05	(D)Py8.5	

* ~0.05 wt. % contribution of Fe interference has been subtracted from Co values.