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DISTRIBUTION OF SELECTED TRANSITION AND HEAVY METALS IN CLASTIC OVERBURDEN UNITS OF THE APPALACHIAN AND INTERIOR COAL BASINS: WATER QUALITY IMPLICATIONS

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DISTRIBUTION OF SELECTED TRANSITION AND HEAVY METALS IN CLASTIC OVERBURDEN UNITS OF THE APPALACHIAN AND INTERIOR COAL BASINS: WATER QUALITY IMPLICATIONS

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ABSTRACT

As part of a study to investigate possible sources of transition and heavy metals transported in coal mine drainage, overburden lithologies from 18 surface mines in the Appalachian and Interior Basins were sampled and analyzed for total chemistry. The mines were widely scattered geographically so that samples could be obtained of as many representative lithologies as possible. Overburden units were predominantly Pennsylvanian basin margin clastics, with some Pennsylvanian carbonates and Pleistocene sediments in the Interior Basin. Based on lithologic descriptions, relative percentages of silicon and aluminum, and gross mineralogy from semi-quantitative X-ray diffraction, the average metals concentrations for overburden units were developed for two major lithologic groups: (1) quartz-rich units, including sandstones, siltstones, and silts; and (2) clay-rich units, including shales, claystones, clays, and tills. Comparing the regional averages for this study with published averages for the coals of the two regions, the highest average concentrations of most metals occurred in the fine-grained (clay-rich) units of the two regions; exceptions were chromium, strontium, and lead in Interior Basin quartz-rich units; and zinc and sulfur in Interior Basin coals. Manganese concentrations were elevated in the quartz-rich units of both regions. In general, the Interior Basin quartz-rich units and coals contained high average

concentrations of iron and sulfur; however, substantial quantities of neutralizers (reflected in high average calcium content and high neutralization potential) were also present in the Interior Basin clastics. Scattergrams of total elemental concentrations indicated that the data for most pairs of elements tended to cluster in particular portions of the field. The most prominent linear trend was a positive relationship between potassium and aluminum for the quartz-rich rocks, where the two occur together as muscovite/illite and K-feldspar. The plots of alkali and alkaline earth metals were the most distinctive for regional discrimination between groups of samples. Scattergrams of average overburden concentrations vs. average untreated mine water concentrations at the various sites were inconclusive. Two better means of evaluating the relationship between overburden chemistry and resulting water quality at coal strip mines are (1) the simple acid-base account and (2) metals concentrations in selected extracts of overburden materials at pH ranges comparable to those in the natural mine setting.

BACKGROUND AND ACKNOWLEDGMENTS

A U.S. Department of Energy (DOE)-funded environmental monitoring study of water quality at 21 coal strip mines in the Appalachian and Interior Basins led to the accumulation of detailed analytical data on overburden chemistry at 18 of the mines studied. The main concern for water quality at surface coal mines, that is, pyrite oxidation and hydrolysis that produces high levels of acidity, sulfate, and dissolved metals in mine waters, is well documented (Singer and Stumm, 1968; Stumm and Morgan, 1970). Overburden analyses usually consist of total chemistry of digested samples, and no attempt is made to simulate the range of water quality conditions at a given mine -- either for comparison of existing water quality with the geologic materials present or for prediction of future water quality. Thus, four of this project's goals were to: (1) examine the total chemistry of overburden materials on a regional basis; (2) compare and contrast the total chemistry of overburden materials with observed water quality; (3) compare the total chemistry of sediments in strip mine settling ponds to overburden chemistry; and (4) analyze a series of aqueous extracts of the pond samples taken under various pH conditions in order to examine the relative mobility of selected metals in the pond sediments. Locations of overburden, water, and sediment pond samples are shown in Figure 1.

The project work was a team effort by many organizations and individuals. The water and overburden sampling and analyses were performed mostly by university and geological survey subcontractors to Argonne National Laboratory (ANL), who are acknowledged individually in Table 1. The assistance of all is gratefully appreciated. Their analyses were supplemented by ANL laboratory work. The averaged coal analyses for the Appalachian and Interior Basins were taken from the U.S. Geological Survey (USGS) open-file report of Swanson and others (1976) and from the Illinois State Geological Survey (ISGS) circular by Gluskoter and others (1977), since coal data were not complete for the Argonne study. The settling pond sediment data (totals and extracts) and the acid-base account for Mine PA1 were completed at the laboratory of the Coal Extraction/Land Reclamation Group at Argonne. Sediment samples were collected by the authors. Laboratory staff whose sample preparation and analytical work was vital to this project include John Freeman, Ann Zoeller, Melvin Findlay, Marilyn Master, and Robert Voss. X-ray diffraction work and initial chemical work on the

and initial chemical work on the settling pond sediments (totals and buffered pH extracts) were completed by Dr. Robert Doehler of Northeastern Illinois University, who was a visiting professor at ANL during the academic year 1977-1978 and was an integral part of the project team. The assistance of Paul Smedinghoff, James McIntyre, Paul Kalisz, and Madeline Antos with data storage and manipulation is also gratefully acknowledged. Funding was provided by U.S. Department of Energy, Division of Environmental Control Technology.

METHODS

Overburden samples consisted mainly of representative grab samples of the various lithologies present at each site; some channel sampling was done at selected sites for both overburden and coal. Digestion methods for overburden analysis used by the university and geological survey subcontractors included acid digestion, lithium metaborate fusion, lithium metaborate/lithium tetraborate fusion, and sodium hydroxide fusion. Detection was by atomic absorption spectrophotometry (AAS) and microprobe analysis. All methods are summarized in Table 1.

Settling pond sediment samples consisted of composite grab samples of the entire sediment column collected as near as possible to the centerline of the delta entering the pond. Samples were stored in plastic bags, kept cool until return to the laboratory, and air dried. For total analysis, the sediment pond samples were digested by lithium metaborate/lithium tetraborate fusion and analyzed by AAS (Shapiro, 1975). The various extracts were done as follows:

Nonbuffered extracts (pH 2.0, distilled water,
pH 10.0): Method of Jackson (1958), using
1:2 Soil:Water Extraction of Soluble Salts.

Buffered extracts (pH 3.4, pH 4.0, pH 5.0, pH 5.9): Method of Gottschalk (1959), using 10mL of a mixture of 2M sodium acetate and 2M acetic acid; the mixture was diluted to 100 mL, shaken with 2 g of sample for 2 days, centrifuged at 2000 rpm for 20 minutes, and the supernatant decanted for analysis.

DTPA extract: Method of The Council of Soil Testing and Plant Analysis (1974) for Determination of Zinc, Manganese, Iron, and Copper by DTPA Extraction.

Analysis of all extracts was by AAS.

The acid-base account for the overburden section at mine PA1 was calculated from acid potential and neutralization potential values determined according to the method of Sobek and others (1978). Carbon and sulfur analyses of overburden and sediment samples were done by LECO furnace; pH was determined in the laboratory using a saturated paste of the ground sample. Analysis of untreated mine waters by the subcontractors detailed in Table 1 was done by AAS according to standard methods using filtered (0.45 μm) samples.

RESULTS AND DISCUSSION

Regional elemental averages for overburden samples were calculated for the two major lithologic groups characteristic of both the Appalachian and Interior Basins; these groups were (1) the quartz or silicon-rich rocks, including sandstones, sands, siltstones, and silts, and (2) clay or aluminum-rich rocks, including shales, claystones, clays, underclays, and tills. Because of the diversity of the data, lithologic descriptions were heavily relied upon, supplemented by semiquantitative X-ray diffraction using pure quartz and clay standards to give relative percentages of each and the ratio of silicon to aluminum for all samples for which major elements were determined. The justification for this broad subdivision of units is shown in Figure 2, a plot of silicon vs. aluminum for the overburden analyses. This indicates a bimodal distribution between samples in which there is a fixed ratio between silicon and aluminum (the linear trend), which we interpret to be clay-dominated, and a cluster of samples in the higher range of silicon values, which we interpret to be quartz-dominated. Elemental analyses performed on carbonates sampled in the Interior Basin are not reported in this paper; however, it should be noted that the highest average concentrations of zinc and accompanying high lead concentrations were characteristic of the few Interior Basin limestones sampled for this study. In glaciated areas within the Interior Basin, the local source material, of course, included Pennsylvanian bedrock; thus, the fine-grained glacial tills are included with the clay-rich lithologic group. Water-laid Pleistocene sediments (silts and sands) were included with the quartz-rich lithologic group. Alluvial and colluvial sediments were likewise categorized according to textural class. Thus, this study basically compares average elemental analyses of basin margin clastics in the Pennsylvanian sequence in the Interior Basin to those in the Appalachian Basin; the few Pleistocene samples that are included mainly serve to increase the data spread in the Interior Basin.

Figures 3 and 4 are bar graphs illustrating a comparison of the results obtained with the average values of sandstone and shale, respectively, reported by Turekian and Wedepohl (1961). These figures plot major and minor elements by percent at the top of each figure and trace elements in parts per million (ppm) at the bottom of each figure. The number of values averaged is given as a range (lowest number of value $\leq$ n $\leq$ highest number of values). Standard deviations were large, as would be expected for this gross type of regional comparison.

Looking first at the clay-rich units in the Appalachian Basin compared to the average shale, it can be seen that these units contained less calcium, magnesium, and sodium, but more potassium, iron, and sulfur. Manganese was about the same as the reported average for shale. In the trace elements, the averages for the Appalachian clay-rich units were all higher than the average shale with the exception of strontium, which was lower. Averages for clay-rich units in the Interior Basin indicated less calcium and magnesium but more sulfur than the average shale. However, these units contained more calcium, magnesium, and sodium, but less iron and sulfur than the average values for the Appalachian Basin clay-rich units. Manganese was similar for the averages of the two regions. Examining the average trace element concentrations for clay-rich units in the Interior Basin, both copper and zinc values were lower than the average shale. Comparing the trace element averages for clay-rich rocks in both regions, it can be seen that cobalt, molybdenum, cadmium, and lead were all higher for the Interior Basin.

Figure 4 presents comparable data for the quartz-rich rocks of both regions. Compared to average sandstone values, the Appalachian Basin averages were lower for calcium and magnesium but generally higher than the average sandstone values. Comparing the quartz-rich units in the Interior Basin to the average sandstone, the Interior Basin rocks contained more sodium, iron, and sulfur, but generally less of the other major and minor elements than the average sandstone. Compared to the quartz-rich Appalachian averages, the Interior Basin quartz-rich units contained more calcium and iron but less potassium. Examining the trace element averages for the quartz rich units of both regions, all of the Interior Basin averages were higher than the average sandstone, and most Interior Basin averages, including chromium, cobalt, nickel, zinc, strontium, cadmium, and lead, were also higher than the Appalachian Basin averages.

Thus, the data in Figures 3 and 4 generally confirm what is known regarding the Pennsylvanian sediments and mine water quality in the two regions. That is, if average calcium concentrations are used as a carbonate indicator, and iron and sulfur as indicators of potential acidity as oxidizable pyrite, the Interior Basin overburden sequence generally contains more average pyrite but also more potential neutralizers than the Appalachian Basin sequence. It is significant that this observation is applicable to the clastics as well as to more general comparisons of the relative amounts of carbonates in the two sequences.

Figures 5 through 7 present selected elemental averages for the two lithologic groups of each region compared to averages developed by Swanson and others (1976) for the coals of the two regions. Their data included averages of 331 coal samples in the Appalachian Basin and 143 samples in the Interior Basin. There were no samples for Illinois in the average coal values reported for the Interior Basin, but averages reported by Gluskoter and others (1977) for 113 Illinois samples were all lower than the averages reported by Swanson and others for the elements presented in Figures 5 through 7.

Figure 5 presents comparative data for iron, manganese, and sulfur -- iron and sulfur as the "acid producers" for mine drainage, and manganese as the only other metal in mine drainage directly regulated by the U.S. Dept. of Interior's Office of Surface Mining (OSM). Manganese also tends to exhibit geochemical behavior similar to that of iron. In Figure 5, iron is highest in the Appalachian clay-rich units, but average iron values are higher in the Interior Basin for both the coals and the quartz-rich rocks. Manganese, unlike many of the metals shown in the figures, is highest in the quartz-rich units in both regions. Total sulfur values are highest in the coals. Comparing the iron and sulfur values stoichiometrically as FeS_2, there is excess iron in the overburden units but approximately the correct ratio by weight in the coals of the two regions. The other major iron mineral present in the overburden is siderite.

Figure 6 presents comparative data for the potential "neutralizers" in the four rock classes plus the coals. Obviously, the highest average percentage of calcium occurs in the Interior Basin; certainly, some of the calcium occurs as gypsum or other minerals in addition to calcite or dolomite (magnesium generally followed calcium in Figures 3 and 4). Note that for calcium in both regions there is a consistency in that calcium is highest in the quartz-rich rocks, next highest in the clay-rich rocks, and lowest in the coals. Strontium generally correlates well with calcium but here the only instance where the relative highs and lows are in phase is for the quartz-rich units, i.e., higher strontium in the Interior Basin. The last set of graphs in this figure illustrates neutralization potential (N.P.), which is the amount of HCl that a given amount of ground rock sample will neutralize (Sobek et al., 1978); the units are tons of calcium carbonate equivalent per 1000 tons, which basically expresses the result as an agricultural lime requirement since 1000 tons is approximately equal to an acre plow layer. The N.P. highs and lows generally follow calcium for the two types of units, as would be expected.

Figure 7 presents equivalent averages for eight selected trace metals. These averages are all higher in the overburden than in the coal with one exception, zinc in Interior Basin coals. These averages are generally higher for the clay-rich rocks than for the quartz-rich rocks for each region: exceptions are zinc, lead, and chromium in the Interior Basin, which were all higher in the quartz-rich units. The molybdenum data averages are somewhat suspect since there were fewer analyses averaged, and thus poorer distribution of results in comparison to accompanying analyses for other elements. The relative averages for trace metals in the quartz-rich rocks generally follow the same trend as iron and sulfur, i.e., higher averages for the Interior Basin than for the Appalachian Basin; the exception is copper. For the clay-rich rocks, recalling that the averages for iron and sulfur were higher in the Appalachian Basin than in the Interior Basin rocks, the same is true only for zinc, nickel, and copper in Figure 7. For the coals of the two regions, recalling the average iron and sulfur were higher in the Interior Basin than in the Appalachian Basin, the same is true for most of the eight metals plotted in Figure 7; the exceptions are chromium and copper.

To summarize the average elemental analyses plotted in Figures 5 through 7, the highest average concentrations of iron, sulfur, zinc, and nickel occur in the quartz-rich rocks and in the coal in the Interior Basin samples; the highest averages for the clay-rich rocks occur in the Appalachian Basin samples. Secondly, for each region, the highest average concentrations of transition and heavy metals occur in the clay-rich units rather than in the quartz-rich units of the coals; exceptions are iron, zinc, lead, and chromium in the Interior Basin and manganese in both regions. Finally, appreciable quantities of potential neutralizers (based on average calcium percent and N.P.) are contributable from calcareous clastics in the two regions; as shown in Figure 6, the resulting averages for these two parameters were substantially higher for the Interior Basin than for the Appalachian Basin.

In an effort to gain insight into the mineralogical combination of the various elements for which average analyses have been presented, scattergrams were plotted for the various elements of each lithologic group. Figure 8 presents generalizations of some of the more meaningful plots. The strongest direct correlation was between aluminum and potassium for the quartz-rich units, where the two elements occur together as muscovite/illite and, locally, as K-feldspar. Other correlations suggested by these plots include, for the clay-rich units, a direct relationship between calcium and magnesium, direct relationships between potassium, aluminum, and silicon, and a cluster of high sodium values for the eastern Interior Basin samples (mostly samples from Mine IN1). In addition, for the clay-rich units, regional separations based on plots of selected alkali and alkaline earth metals, mainly relating to the wide range of higher calcium and magnesium values for the samples from the Interior Basin, were also evident. For the quartz-rich units, the strong potassium/aluminum relationship was also suggested in the plot of potassium vs. magnesium. Regional separations for the quartz-rich samples were also evident for selected metals -- including nickel vs. copper and zinc. In general, however, the plots of alkali and alkaline earth metals, apparently relating to regional paleoenvironmental considerations, were the most meaningful for data separations between basins.

Prediction of mine water quality from the types and quantities of overburden materials present is a tenuous exercise at best. To examine possible relationships between total chemistry of overburden material and raw water quality at the sites studied, scattergrams were also plotted of average concentrations of overburden constituents at each site vs.

average pit water quality; these were generally inconclusive. Two methods which have more promise are illustrated in Tables 2 and 3. The first table presents manganese analyses from five samples taken from settling ponds which receive pumped discharges from the active pit at some acid Appalachian strip mines in Maryland, West Virginia, and Pennsylvania. The mine effluent at all five sites required chemical neutralization treatment before discharge. The settling pond sediments were chosen as a worst-case condition since they are the most fine-grained and homogeneous of the overburden-derived spoil materials; they may also contain high levels of transition and heavy metals. Some of these metals are overburden-derived, some are contributed directly from local erosion, and others are taken out of the water by direct precipitation, co-precipitation, and/or adsorption. Figure 9 is a plot of silicon vs. aluminum for pond sediments at mines requiring chemical neutralization treatment for water; note the similarity to the same plot for the overburden materials (Figure 2), indicating a population split into clay-dominated and quartz-dominated factions. For unmined areas, a similar set of analyses can be performed on representative overburden samples from exploratory drilling. The data for manganese are presented here because, although manganese is not particularly toxic, it was the most mobile of the metals studied, and other metals tended to mirror its behavior to a greater or lesser extent. Table 2 also presents some basic characteristics of the five samples chosen; note the diversity of values for pH, sulfur, carbon, N.P., and clay, with MD1-7 being highest in clay and PA3-1 highest in sulfur, and lowest in pH and N.P. The data for the various extracts indicate the various amounts of manganese released as a result of three types of laboratory extraction procedures at various pH levels. The first column shows the total amount of manganese present, in weight percent. The next three columns indicate the parts per million of manganese extracted (dry weight sediment basis) by non-buffered aqueous extracts (2:1 water: sediment) at a low pH (2.0 using HCl), a near-neutral pH (using distilled water), and a high pH (10.0, using NaOH). Columns five through eight show the amount of manganese extracted with sodium acetate/acetic acid buffer solutions at pH 3.4, 4.0, 5.0, and 5.9. The second-to-last column shows the amount of manganese extracted with the chelate DTPA (diethylenetriamine pentaacetic acid). Finally, for comparison, the last column gives averages and ranges for manganese concentrations in the water overlying the pond sediments, and also the pH ranges for the pond water (which were extreme). Note that there was generally an inverse relationship between extractable manganese concentrations and pH in both the buffered and nonbuffered systems. It is generally true that the highest amounts of manganese (and the other metals) extracted occurred in the buffered system. Within the buffered system, the highest amounts of manganese (and most other metals) extracted occurred for sample PA1-1, which had the most manganese (and other metals) present on a total basis. In the nonbuffered system, the highest amounts of manganese extracted occurred for sample PA3-4, which was the most acid (lowest pH and N.P.), even though it had the least total amount of manganese present. The DTPA extractable manganese, included to consider the potential success of pond reclamation since it generally correlates well with plant uptake as a measure of exchangeable metals, was highest for the same sample as the buffered extracts (PA1-1, the sample with the most total manganese present).

Some tentative conclusions for the pond sediments, based on the preliminary but rather extensive set of extracts completed for the five samples in Table 2 include:

1. The behavior of manganese, as just described, was essentially duplicated by cobalt, nickel, copper, zinc, and cadmium.
2. The behavior of chromium generally showed the same behavior as manganese for the nonbuffered extracts (i.e., most extracted in the two most acid samples), but showed a correlation with clay content in the buffered extracts (most extracted in sample MD1-7).
3. The behavior of iron and lead showed the same behavior as manganese in the nonbuffered system; however, there were generally higher amounts of iron and lead extracted in the buffered system for sample PA3-4, the most acid sample.
4. Actual pond-water concentrations (mean and range given in last column) generally were of the same order of magnitude as the nonbuffered water extracts, but the wide range of average manganese concentrations for pond water (less than 1 to more than 60 mg/L) reflects the wide range of pond acidity through a given year.
5. Among the low pH buffered extract (pH 3.4), the low-pH nonbuffered extract (pH 2.0), and the DTPA extract, there was a remarkable consistency in the order of elements extracted (calculated on a percent-of-total basis). The order was (manganese) > (nickel,zinc, cobalt) > (chromium,copper,iron,aluminum).

The implications of the aqueous extracts performed on the sediment samples with regard to mine water quality are obviously preliminary but present some interesting possibilities. For example, the fact that the high amounts of metals extracted in the buffered system were rarely observed in the pond waters suggests that the time required for the sediment/pond-water system to reach some sort of dynamic equilibrium is never attained in the natural setting. Rather, due to periodic influxes of acid untreated water and treated, sometimes highly alkaline, water, many metals undergo rapid flux from the liquid to the solid state. As a result, the metals concentrations in pond waters seemed to average close to those of a distilled water extract. If there were prolonged contact of pond materials with low pH waters, metals concentrations might reach extreme levels. Another interesting observation to be made regarding the metals data for the pond sediments is the mobility of manganese, which is one of the four mine drainage parameters regulated by OSM. Often, simple chemical neutralization treatments (hydrated lime, soda ash), effectively reduce iron concentrations in mine drainage but do not reduce manganese concentrations to acceptable levels. The preliminary data here suggest that manganese, due to its mobility, may indeed be a good indicator of high levels of other metals in mine drainage since the other metals tended to mirror its behavior.

Table 3 shows an example of what is still probably the best predictor of water quality at coal strip mines, a simple acid-base account of an overburden section (Mine PA1) in which an excess or deficiency of bases is reported for each unit. The basic data for the construction of this account consists of two measurements for each unit: total (or pyritic) sulfur, and neutralization potential. The accounting balances maximum potential acidity (from immediately-titratable sources as sulfuric acid equivalent) against total neutralizers (from alkaline carbonates, exchangeable bases, weatherable silicates, or other sources capable of neutralizing strong acids as determined by the N.P.). The potential acidity is determined by multiplying the total or pyritic sulfur content of a rock unit (given in %) by 31.25, since overburden material containing 1% sulfur (all pyritic) will require 31.25 tons of calcium carbonate to neutralize the sulfuric acid produced by oxidation and hydrolysis of 1000 tons of the overburden material. Thus, the N.P. is balanced against potential acidity to form a net acid-base account. The excess or deficiency of bases for each unit can then be multiplied by unit thicknesses to indicate approximate quantities of acidic vs. neutral-to-alkaline spoil materials. See Sobek and others (1978) for further discussion of this method.

The data for PA1 indicate that sulfur content is highest adjacent to the coals. Most overburden samples, however, contain excess neutralizers -- especially sample B-15. Examining the total thickness of the acid toxic materials (those with a net deficiency of bases), these materials comprise only about 16% of this particular overburden section. Thus, water quality in spoils can be maintained by blending the toxic and nontoxic materials. The main toxic horizons of concern are B-11x, B-10, and B-1x.

The value of an acid-base account is that it is a simple, readily accessible method for mine operators to identify acid-toxic materials in a given overburden sequence and give some indication of the balance between potential acid-producers and potential neutralizers. A detailed exploratory program can thus give an indication, prior to mining, of the relative volumes of both types of materials present. For simplicity, total sulfur values are often used for this accounting, but high concentrations of sulfate or organic sulfur will give misleading results; in such cases, additional leaching of representative samples to determine pyritic sulfur content is frequently desirable.

Thus, one can utilize at least two methods to predict water quality in a given mine setting: (1) the acid-base account to examine the potential of a given unit or a given overburden sequence for acid/neutralization potential, and (2) aqueous extracts to simulate the release of various metals under a range of pH conditions. A full characterization of an overburden sequence will include both types of analyses. As indicated by the relative amounts of metals present on a total basis and the amounts of metals extracted from the settling pond sediments by the buffered pH solutions, time is the unknown but critical factor in predicting water quality. The rate at which acidity and metals are released and acidity is neutralized (either naturally or by chemical treatment) is a function of mining method, spoil handling and placement, and hydrogeologic setting/drainage plan, all of which interact to determine the rate at which the pH-dependent solubilization of metals occurs in a natural mine setting.

REFERENCES CITED

Council of Soil Testing and Plant Analysis, 1974, Handbook of Reference Methods of Soil Testing, pp. 79-83: Determination of Zinc, Manganese, Iron and Copper by DTPA Extraction.

Federal Register, January 12, 1979, Coal Mining Point Source Category, Standard of Performance for New Sources: Vol. 44, No. 9, Part 434, pp. 2586-2592.

Gluskoter, H. J., et al., 1977, Trace Elements in Coal: Occurrence and Distribution: Illinois State Geological Survey Circular 499.

Gottschalk, 1959, Zeit. anal. Chem. 167:342: In Buffers for pH and Metal Ion Control, D. D. Perrin and B. Dempsey, Wiley, N.Y. (1974).

Jackson, M. L., 1958, Soil Chemical Analysis: Prentice-Hall, pp. 249-251.

Shapiro, Leonard, 1975, Rapid Analysis of Silicate, Carbonate, and Phosphate Rocks -- Revised Edition: U.S. Geological Survey Bulletin 1401, pp. 43-46.

Singer, Philip C., and Stumm, Werner, 1968, Kinetics of the Oxidation of Ferrous Iron: Second Symposium on Coal Mine Drainage Research, Mellon Institute, Pittsburgh, Pennsylvania, pp. 12-34.

Sobek, A. A., et al., 1978, Field and Laboratory Methods Applicable to Overburdens and Minesoils: U.S. Environmental Protection Agency EPA-600/2-78-054, Grant No. R803508-01-0, Industrial Environmental Research Laboratory, Cincinnati, Ohio.

Stumm, Werner, and Morgan, James J., 1970, Aquatic Chemistry: Wiley-Interscience, New York.

Swanson, Vernon F., et al., Collection, Chemical Analysis, and Evaluation of Coal Samples in 1975: U.S. Geological Survey Open File Report 76-468.

Turekian, Karl K., and Wedepohl, Karl H., (February 1961), Distribution of the Elements in Some Major Units of the Earth's Crust: Geological Society of America Bulletin, 72:175-192.

Table 1. Methods of Overburden Sample Collection, Digestion, and Analysis; Key to Subcontractors and Mine Drainage Treatment Methods

Site	Type of Sample	Overburden Digestion Method(s)	Overburden Analysis Method(s)	Cooperator(s)	Method of Chemical Neutralization Treatment for Mine Water
1-OH1	C	NaOH Fusion, and HF, H_2SO_4, HNO_3	AAS	Corbett, U. of Akron	None (Na_3CO_3 for coal pile runoff only)
2-AL1	G	$LiBO_2$ Fusion	AAS	Boone and Evans, Ala. Geological Survey	$Ca(OH)_2$, Cl_2, Al_2O_3 (not in use)
3-TN1	G	HF, H_2ClO_4	AAS	Byerly, U. of Tenn.	NaOH (abandoned)
4-TN2	G	HF, H_2ClO_4	AAS	Byerly, U. of Tenn.	None
5-KY1	G	$Li_2B_4O_7$ Fusion	AAS, ES, XRF	Hester and Leung, E. Kentucky U.	None
6-KY2	G	$Li_2B_4O_7$ Fusion	AAS, ES, XRF	Hester and Leung, E. Kentucky U.	None
7-PA1	G	$LiBO_2$ Fusion	AAS, ES	Lovell and Parizek, Penn. State U.	$Ca(OH)_2$
8-PA2	G	$LiBO_2$ Fusion	AAS, ES	Lovell and Parizek, Penn. State U.	None
9-PA3	G	$LiBO_2$ Fusion	AAS, ES	Lovell and Parizek, Penn. State U.	$Ca(OH)_2$, Na_2CO_3
10-MD1	G	$LiBO_2$ Fusion	AAS	Behling and Renton, W. Virginia U.	$Ca(OH)_2$, Na_2CO_3, alkaline industrial waste
11-WV1	G	$LiBO_2$ Fusion	AAS	Behling and Renton, W. Virginia U.	$Ca(OH)_2$, Na_2CO_3
12-KY3	C	HF, H_2SO_4, HNO_3	AAS	Hood, S. Ill. Univ.	NaOH
13-IN1	G	HF, HCl, HNO_3	AAS	Guernsey, Ash, Howe, Siether; Ind. State U.	None

Table 1 (Contd.)

Site	Type of Sample	Overburden Digestion Method(s)	Overburden Analysis Method(s)	Cooperator(s)	Method of Chemical Neutralization Treatment for Mine Water
14-IL1	C	HF, H_2SO_4, HNO_3	AAS	Hood, S. Ill. U.	None
15-IL2	C	HF, H_2SO_4, HNO_3	AAS	Hood, S. Ill. U.	None
16-IA1	G	(sulfur forms, neutralization potential only)		Sendlein, Iowa State U.	$Ca(OH)_2$
17-MO1	G	HF, H_2ClO_4, HNO_3	AAS	Bolter, U. of Mo.	NH_3
18-MO2	G	HF, H_2ClO_4, HNO_3	AAS	Bolter, U. of Mo.	None
19-OK1	G	HCL, HF, H_2SO_4	AAS, wet chemical, XRF, MP	Comer, U. of Tulsa	None

Key to Abbreviations

C = Channel sample
G = Grab sample
AAS = Atomic absorption spectrophotometry
ES = Emission spectrophotometry
XRF = X-ray fluorescence
MP = microprobe

Table 2. Total and Extractable Mn from Selected Settling Pond Sediment Samples

Sample No.	Total Mn Present (%)	Non-buffered			Buffered				DTPA	Average (and Range) for Pond Water [pH range]
		pH 2.0 ppm	Dist H_2O ppm	pH 10.0 ppm	pH 3.4 ppm	pH 4.0 ppm	pH 5.0 ppm	pH 5.9 ppm	ppm	Mg/L [pH]
MD1-7 pH = 5.4 N.P. = 5.0 Tons $CaCO_3$/1000 Tons % C = 5.1 % S = 0.03 % Clay = 35.	0.03	66	14	4.4	95	93	88	56	60	63 (20-96) [2.4-7.0]
WV1-4 pH = 7.1 N.P. = 23 % C = 2.7 % S = 0.07 % Clay = 40	0.08	58	8.6	1.1	429	407	351	218	69	7.8 (2.1-20) [3.9-8.3]
WV2-3 pH = 5.0 N.P. = 1.2 % C = 2.6 % S = 0.01 % Clay = 60	0.07	336	2.0	1.7	412	370	339	311	193	0.73 (0-2.2) [4.4-10.4]

Table 2 (Contd.)

Sample No.	Total Mn Present (%)	Non-buffered			Buffered				DTPA	Average (and Range) for Pond Water [pH range]
		pH 2.0	Dist H_2O	pH 10.0	pH 3.4	pH 4.0	pH 5.0	pH 5.9		
		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	Mg/L [pH]
PA1-1 pH = 7.3 N.P. = 15 % C = 5.1 % S = 0.03 % Clay = 35.	0.17	26	2.9	1.3	1350	1280	1240	906	201	2.2 (0.96-3.7) [4.2-8.7]
PA3-4 pH = 3.5 N.P. = 0.98 % C = 18 % S = 1.1 % Clay = 65	0.03	162	74	13	165	154	167	165	89	20 (15 -27) [2.9-6.7]

Table 3. Acid/Base Account for Mine PA1.

SAMPLE NO.	ROCK TYPE[a]	pH	TOTAL SULFUR PERCENT	$CaCO_3$ EQUIVALENTS (TONS/1000 TONS)			
				MAXIMUM FROM TOTAL SULFUR PERCENT (ACID POTENTIAL)	AMOUNT PRESENT (NEUTRALIZATION POTENTIAL)	MAXIMUM NEEDED (pH 7.0)	EXCESS $CaCO_3$
B–18	ss	5.3	.045	1.4	2.4		1.0
B–17	sh	7.3	.030	.94	28.		27.
B–16x	sh	2.8	2.4	75.	–4.3	79.	
COAL							
B–15	slst	8.2	.087	2.7	280.		280.
B–14	slst	8.1	.025	.78	51.		50.
B–13	ss	5.2	.000	–0–	0.07		0.07
B–12	slst	7.5	.093	2.9	32.		29.
B–11x	sh	2.9	8.6	270.	–6.5	280.	
COAL							
B–10	sh	3.7	1.2	37.	.36	37.	
B–9	slst	4.4	.080	2.5	11.		8.5
B–8x	sh	3.1	.690	22.	.21	22.	
COAL							
B–7	sh	4.3	.068	2.1	1.5	0.6	
B–6	uc	6.6	.030	.94	25.		24.
B–5	sh	6.2	.010	.31	2.4		2.1
B–4	slst	7.6	.020	.63	29.		28.
B–3x	sh	7.2	.025	.78	4.0		3.2
B–3	ss	4.3	.19	6.0	–0.29	6.3	
B–2	slst	7.5	.035	1.1	19.		18.
B–1x	sh	3.3	1.7	53.	–0.76	54.	
COAL							

[a] ss = SANDSTONE
sh = SHALE
slst = SILTSTONE
uc = UNDERCLAY

Fig. 1. Overburden, Water, and Sediment Sampling Sites.

Fig. 2. Plot of Silicon vs. Aluminum.

Fig. 3. Average Overburden Chemistry of Quartz-rich Units Compared to Average Sandstone.

Fig. 4. Average Overburden Chemistry of Clay-rich Units Compared to Average Shale.

Fig. 5. Comparative Overburden and Coal Averages for Iron, Manganese, and Sulfur.

Fig. 6. Comparative Overburden and Coal Averages for Calcium, Strontium, and Neutralization Potential.

Fig. 7. Comparative Overburden and Coal Averages for Selected Trace Metals.

Fig. 8. Generalized Scattergrams of Clay-rich and Quartz-rich Overburden Units -- Total Chemical Analysis.

Fig. 9. Scattergram of Silicon vs. Aluminum for Settling Pond Sediments at Mines with Chemical Neutralization Treatment (n = 30).

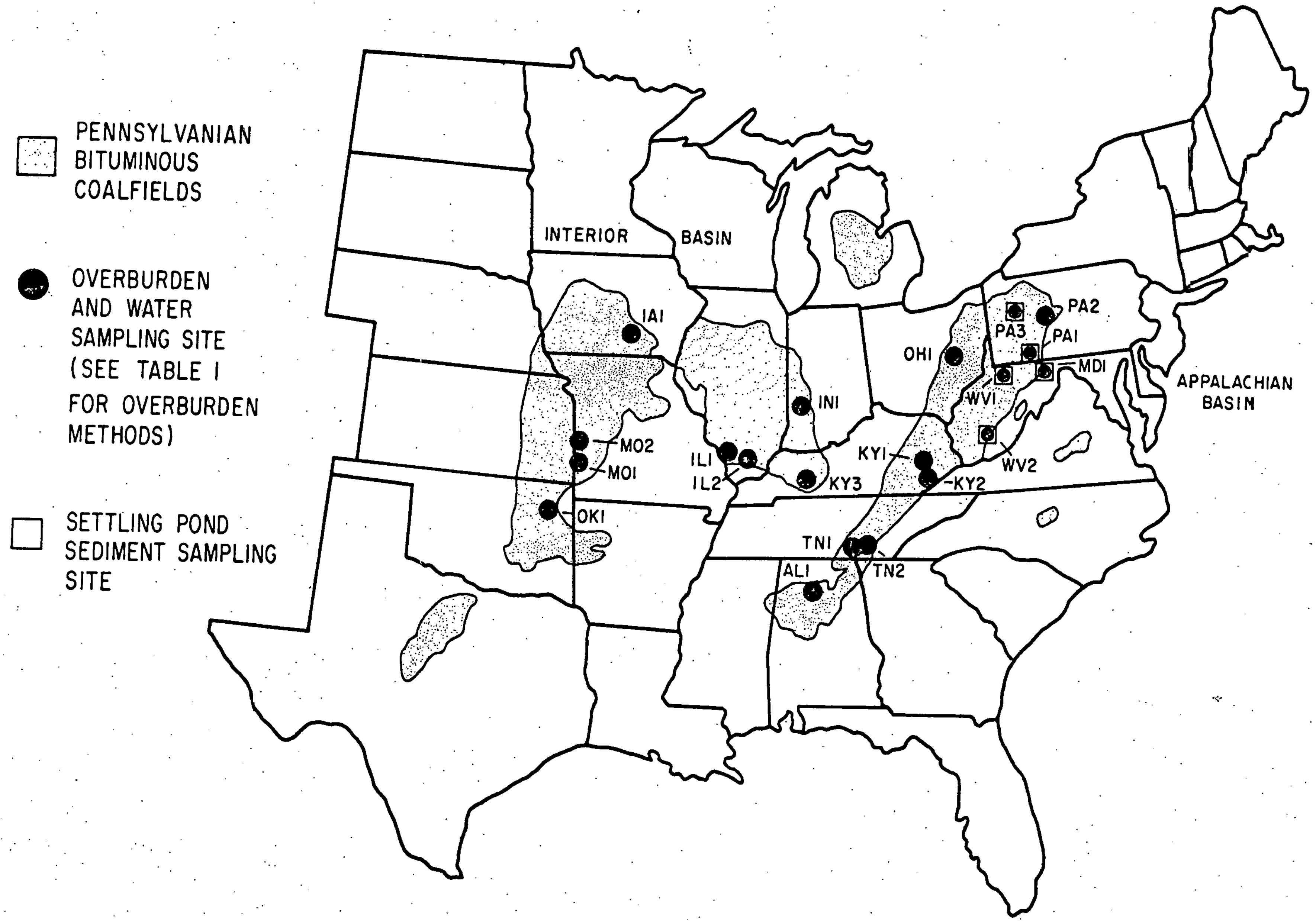
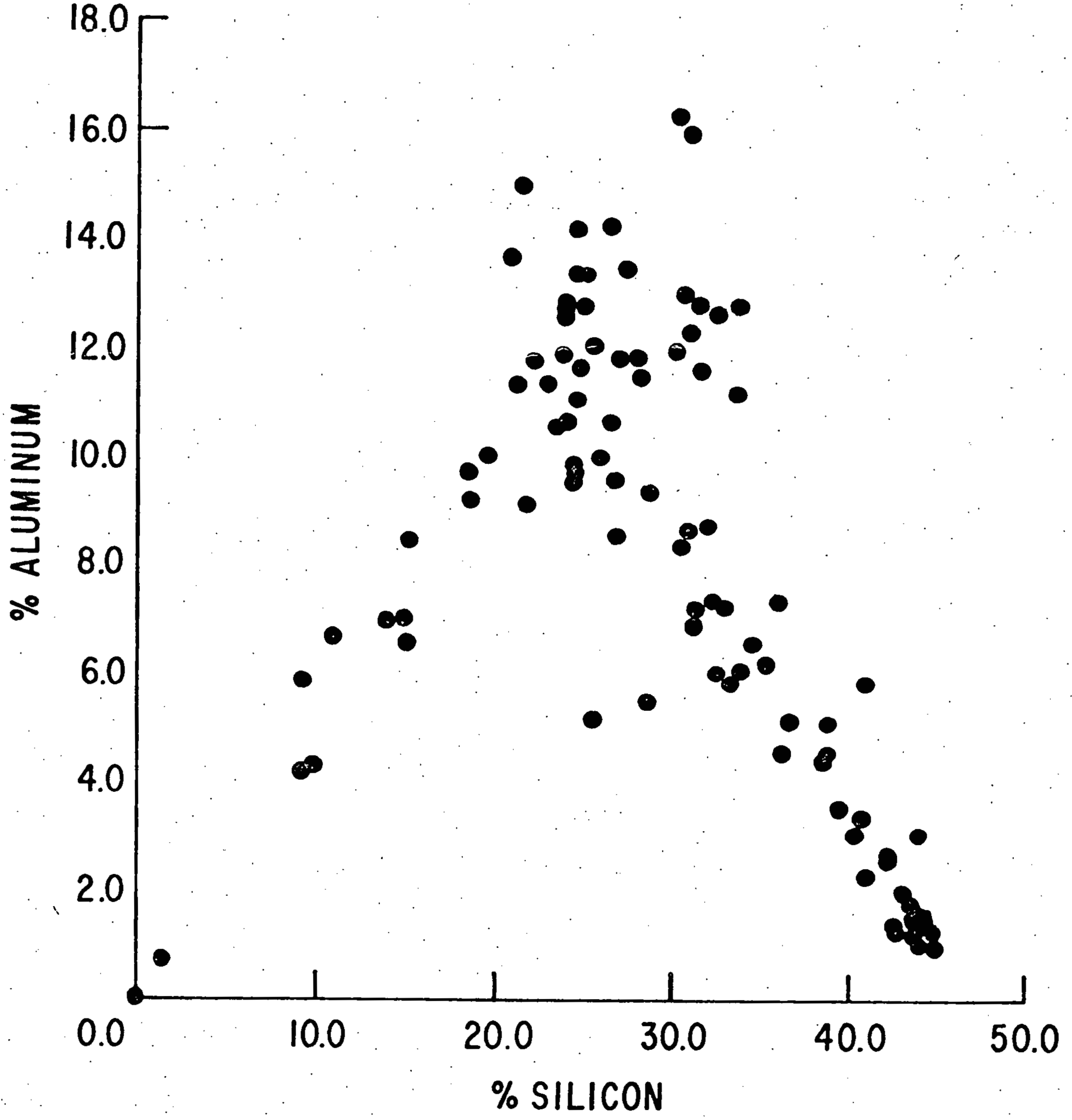

PENNSYLVANIAN BITUMINOUS COALFIELDS
OVERBURDEN AND WATER SAMPLING SITE (SEE TABLE I FOR OVERBURDEN METHODS)
SETTLING POND SEDIMENT SAMPLING SITE
INTERIOR
BASIN
APPALACHIAN BASIN
IA1
IN1
IL1
IL2
KY3
MO2
MO1
OK1
OH1
PA2
PA3
PA1
MD1
WV1
WV2
KY1
KY2
TN1
TN2
AL1

Fig 1

Fig 2

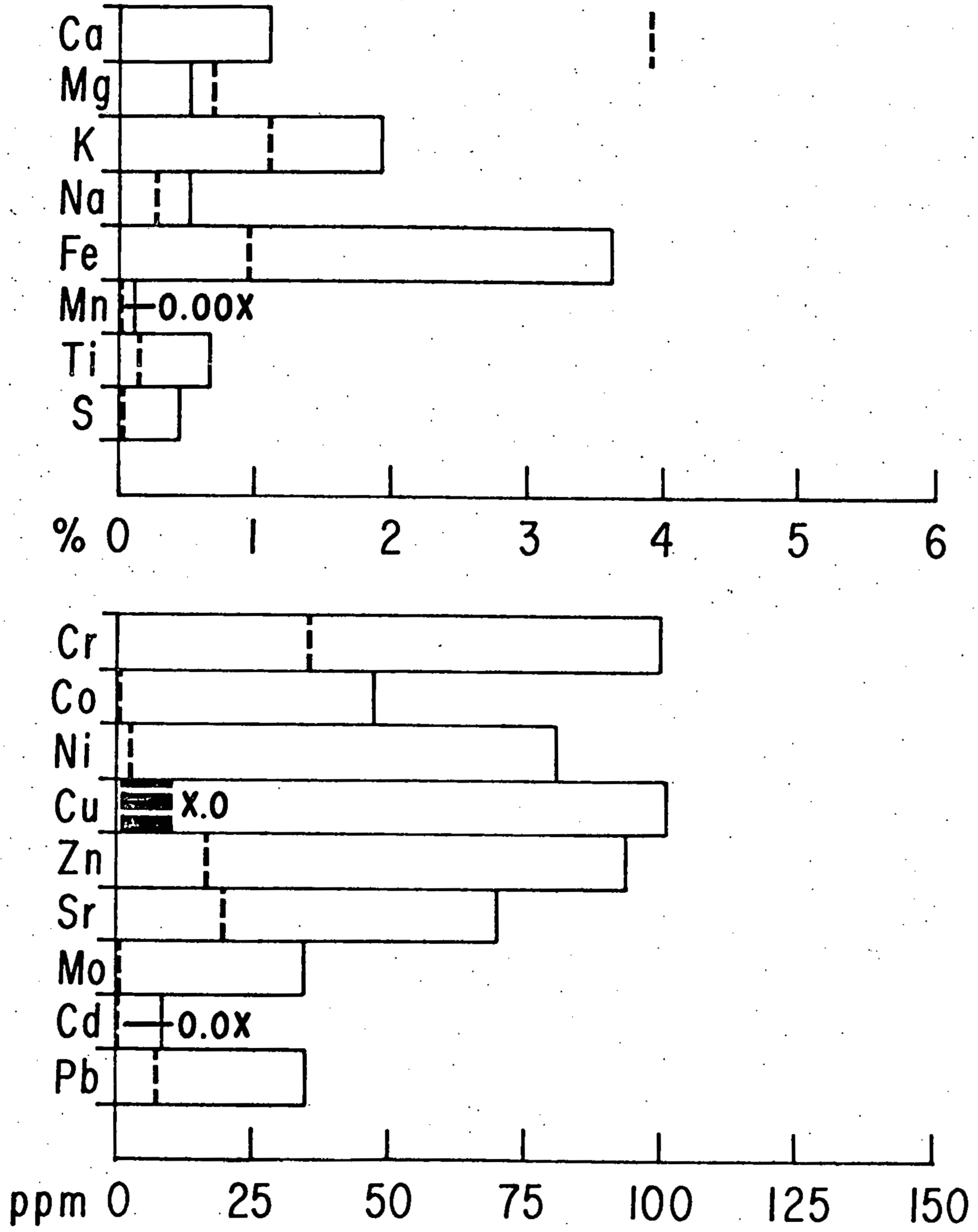


18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
% ALUMINUM
0.0
10.0
20.0
30.0
40.0
50.0
% SILICON

Fig 3 (1)

APPALACHIAN BASIN

$34 \leq n \leq 67$

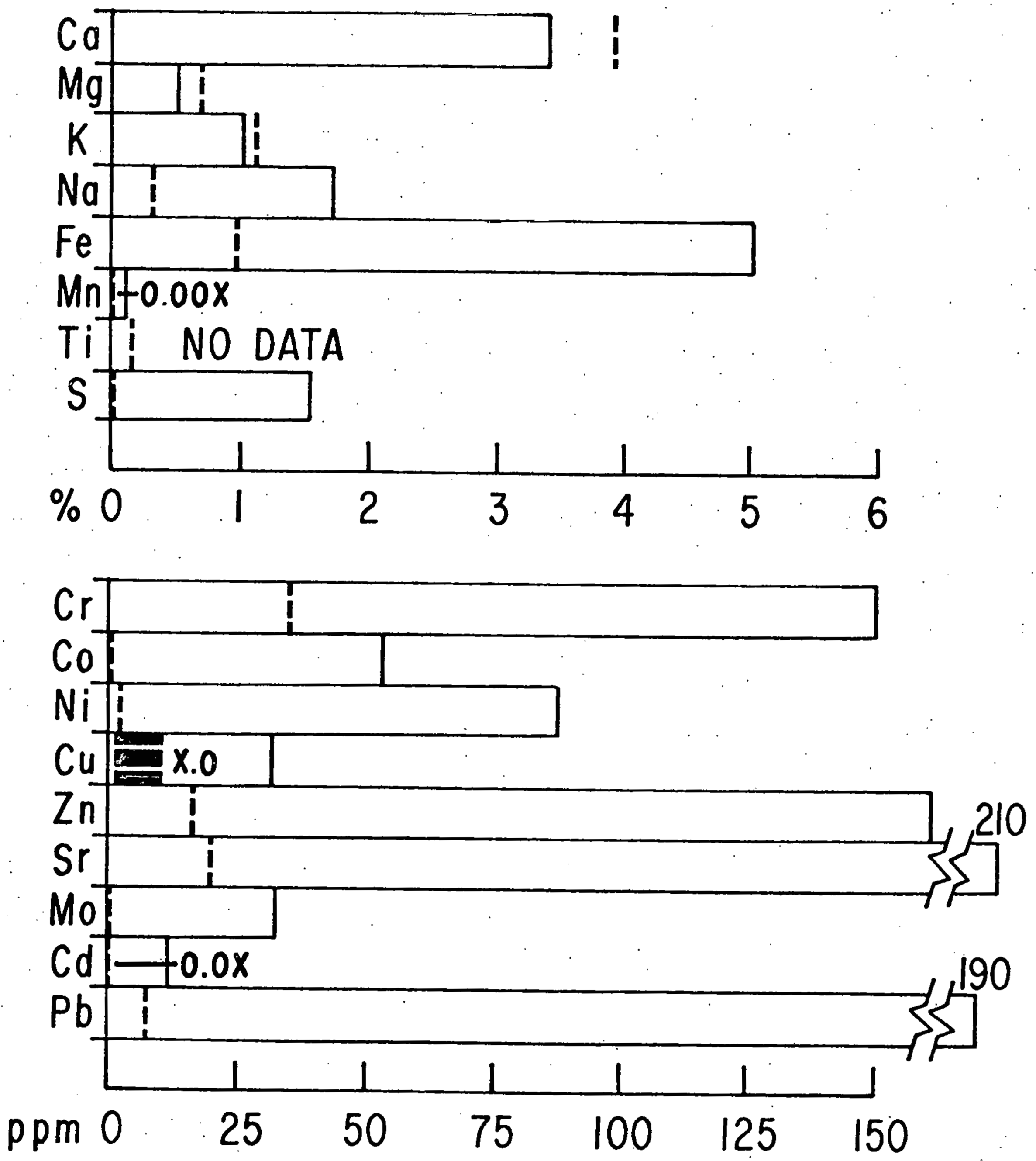


¦ AVERAGE SANDSTONE
(Turekian & Wedepohl, 1961)

x indicates order of magnitude only

Fig 3 (2)

INTERIOR BASIN
$6 \leq n \leq 16$



¦ AVERAGE SANDSTONE
(Turekian & Wedepohl, 1961)

x indicates order of magnitude only

Fig 4 (1)

APPALACHIAN BASIN

$13 \leq n \leq 81$

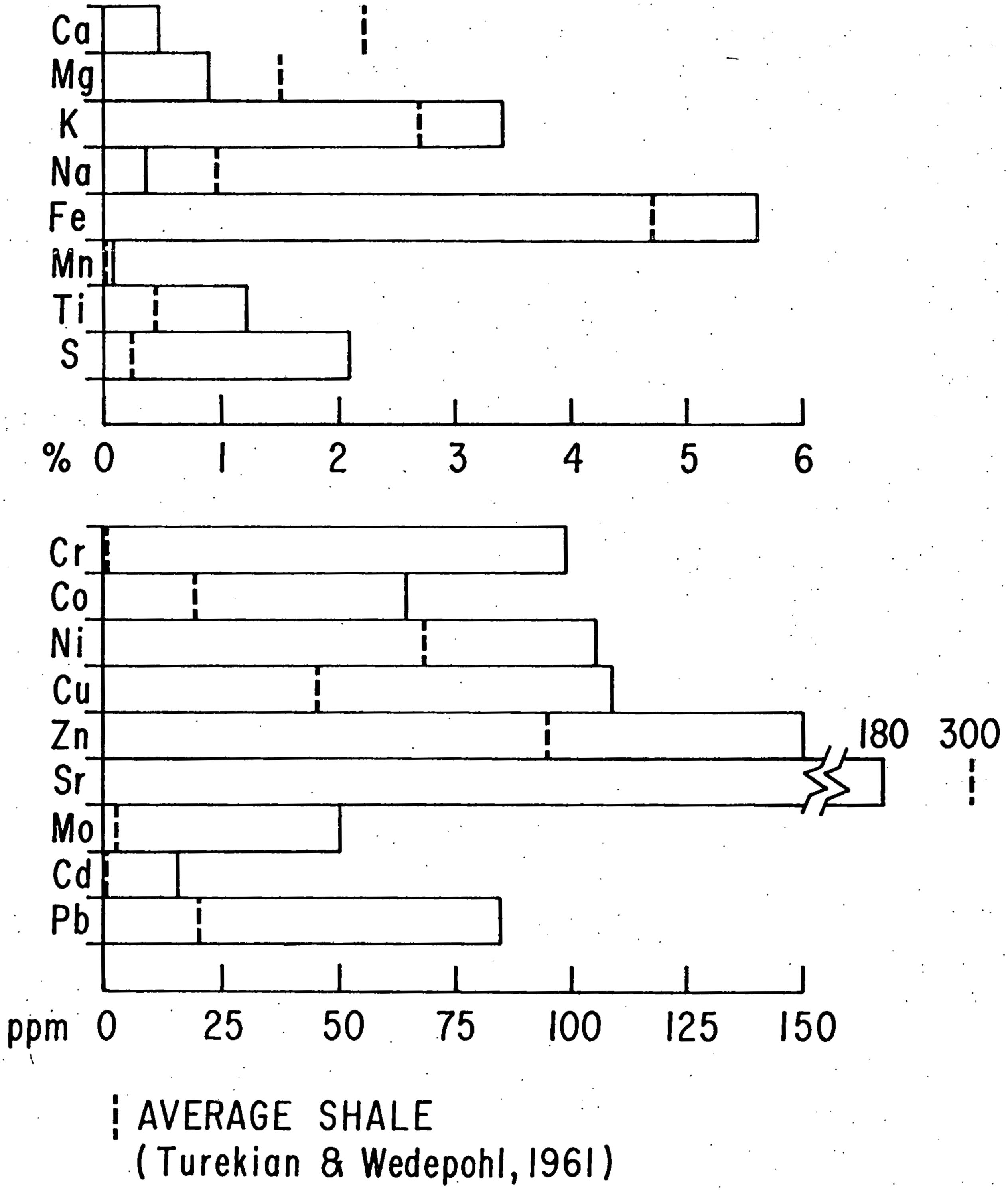
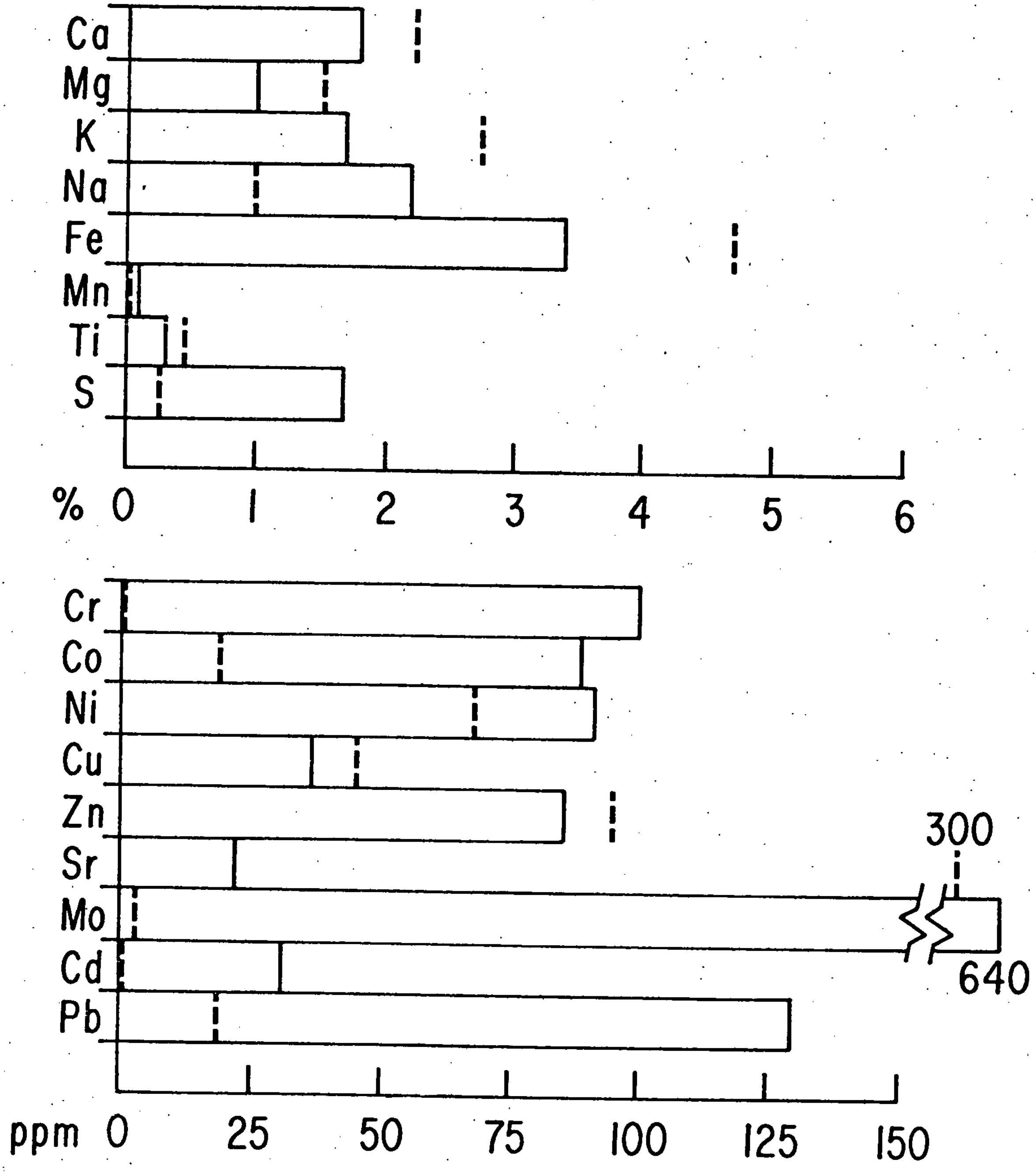


Fig. 4 (2)

INTERIOR BASIN

$3 \leq n \leq 77$



¦ AVERAGE SHALE
(Turekian & Wedepohl, 1961)

Fig 5

Fig 5

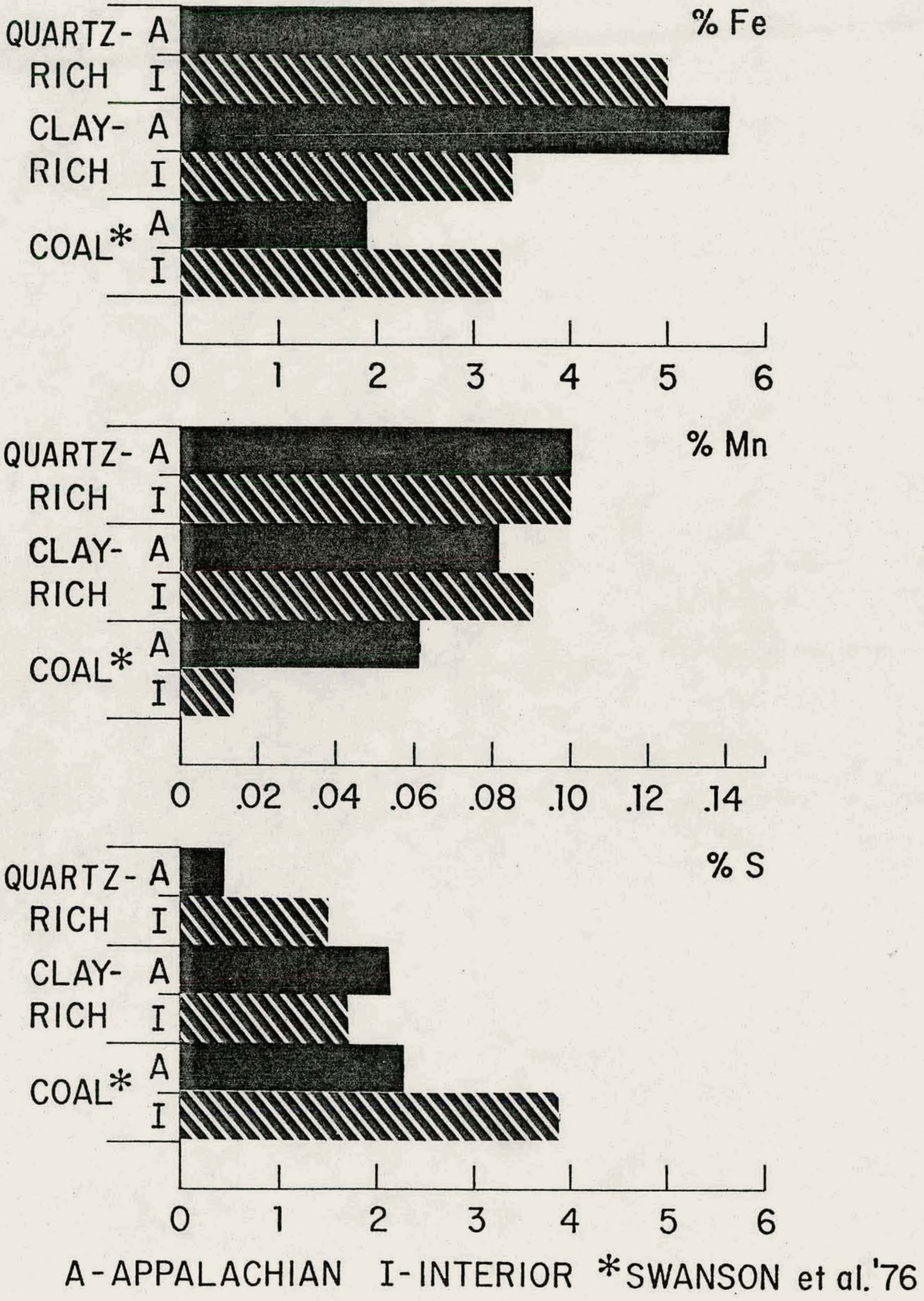
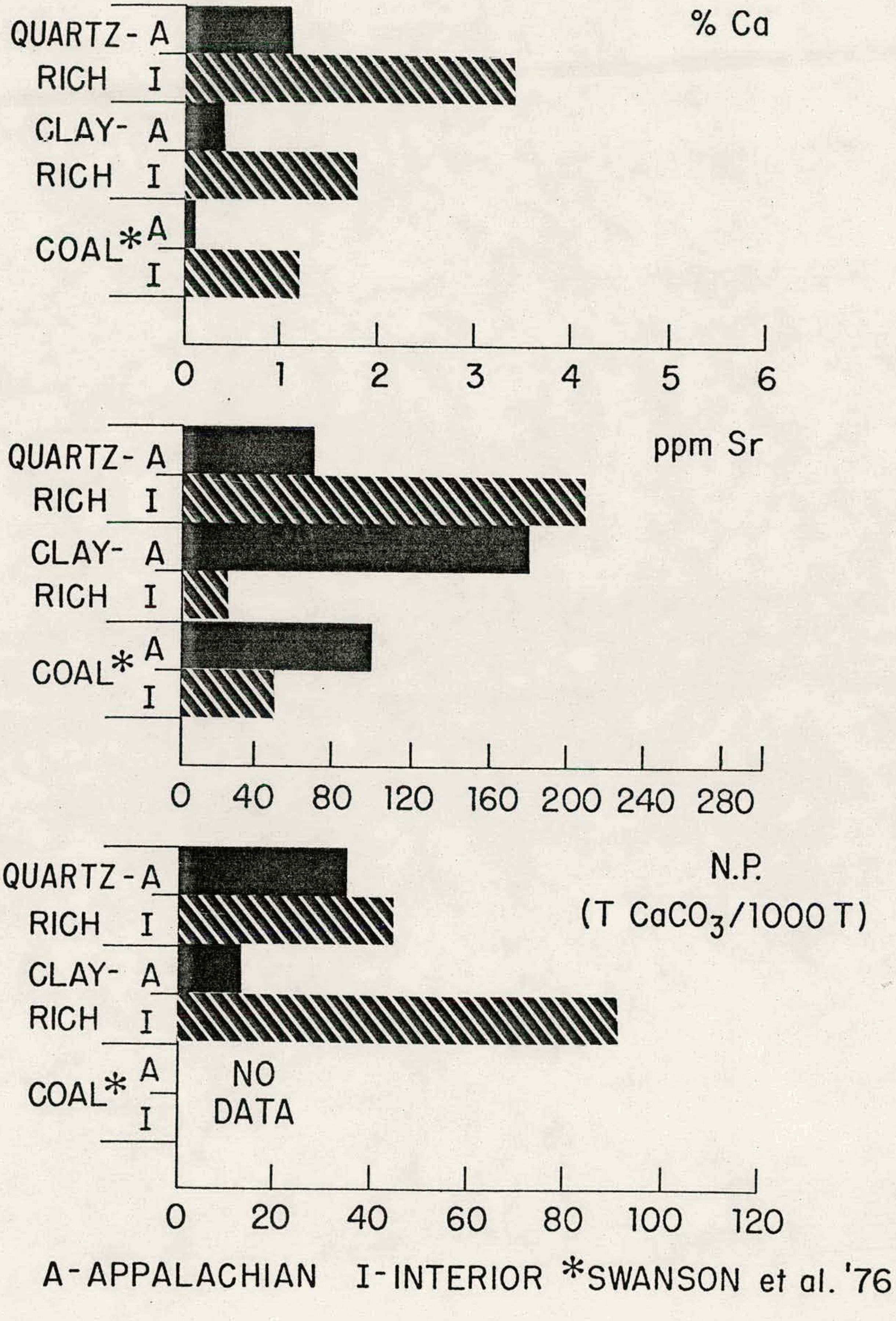

% Fe
QUARTZ- RICH
CLAY- RICH
COAL*
A
I
0
1
2
3
4
5
6
% Mn
QUARTZ- RICH
CLAY- RICH
COAL*
A
I
0
.02
.04
.06
.08
.10
.12
.14
% S
QUARTZ- RICH
CLAY- RICH
COAL*
A
I
0
1
2
3
4
5
6
A-APPALACHIAN
I-INTERIOR
*SWANSON et al.'76

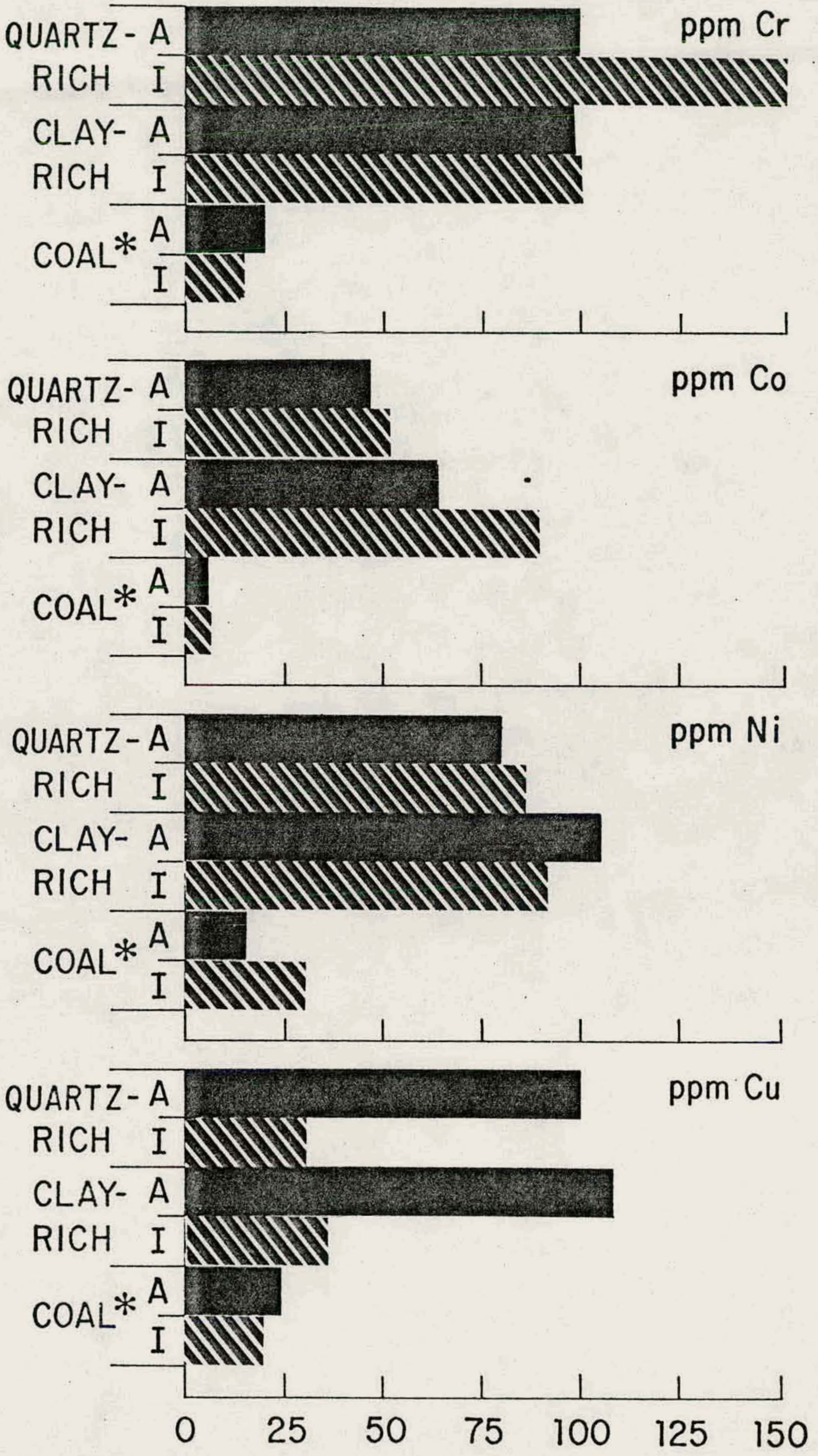
Fig 6 Fig 6



% Ca
QUARTZ- A
RICH I
CLAY- A
RICH I
COAL* A
I
0 1 2 3 4 5 6
ppm Sr
QUARTZ- A
RICH I
CLAY- A
RICH I
COAL* A
I
0 40 80 120 160 200 240 280
N.P. (T $CaCO_3$/1000 T)
QUARTZ- A
RICH I
CLAY- A
RICH I
COAL* A
I
NO DATA
0 20 40 60 80 100 120
A-APPALACHIAN I-INTERIOR *SWANSON et al. '76

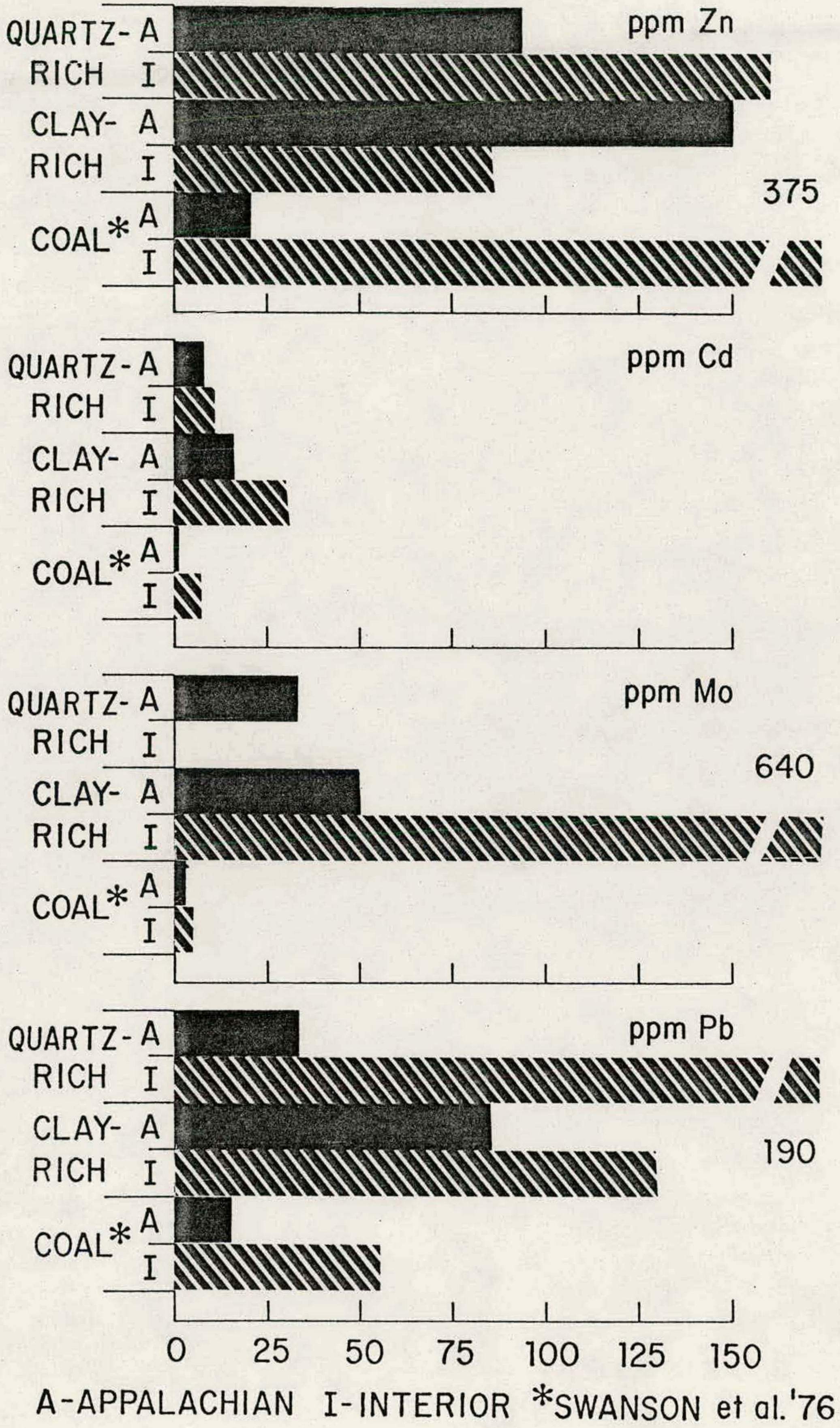
Fig 7

Fig 7 (1)



A-APPALACHIAN I-INTERIOR *SWANSON et al.'76

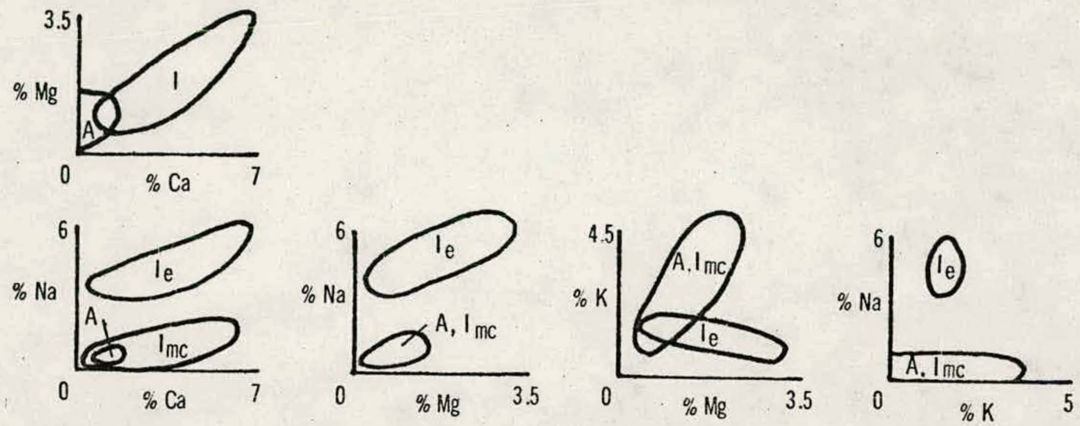
Fig 7 (2)

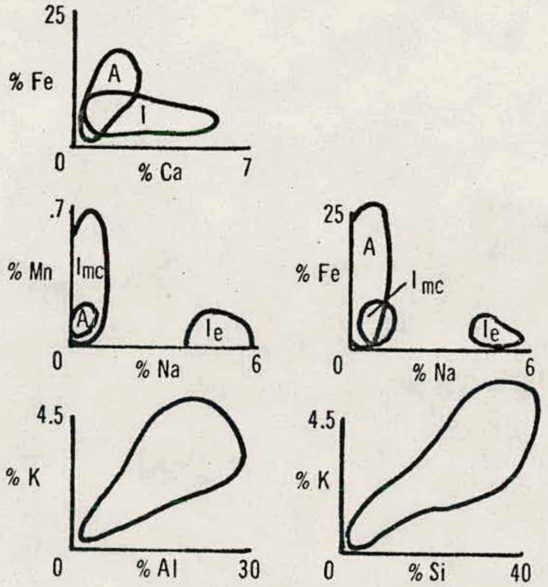


ppm Zn
QUARTZ-RICH A
QUARTZ-RICH I
CLAY-RICH A
CLAY-RICH I
COAL* A
COAL* I
375
ppm Cd
QUARTZ-RICH A
QUARTZ-RICH I
CLAY-RICH A
CLAY-RICH I
COAL* A
COAL* I
ppm Mo
QUARTZ-RICH A
QUARTZ-RICH I
CLAY-RICH A
CLAY-RICH I
COAL* A
COAL* I
640
ppm Pb
QUARTZ-RICH A
QUARTZ-RICH I
CLAY-RICH A
CLAY-RICH I
COAL* A
COAL* I
190
0
25
50
75
100
125
150
A-APPALACHIAN I-INTERIOR *SWANSON et al.'76

Fig 8

CLAY – RICH UNITS:





KEY

A = APPALACHIAN BASIN

I = INTERIOR BASIN, INCLUDES EASTERN INTERIOR BASIN (I_e) AND MIDCONTINENT BASIN (I_{mc})

QUARTZ – RICH UNITS:

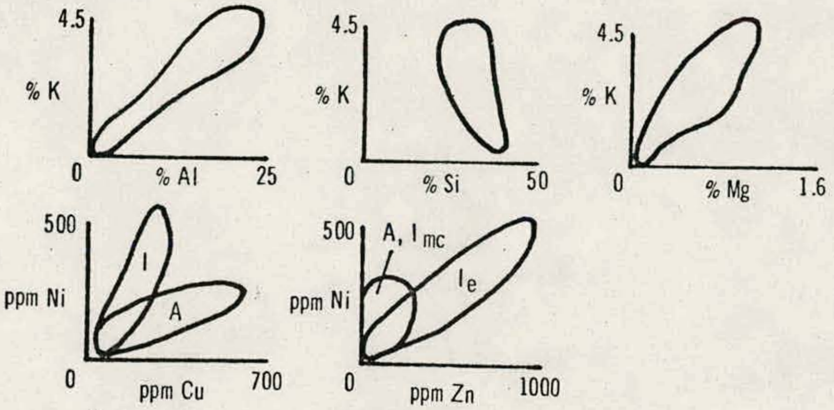
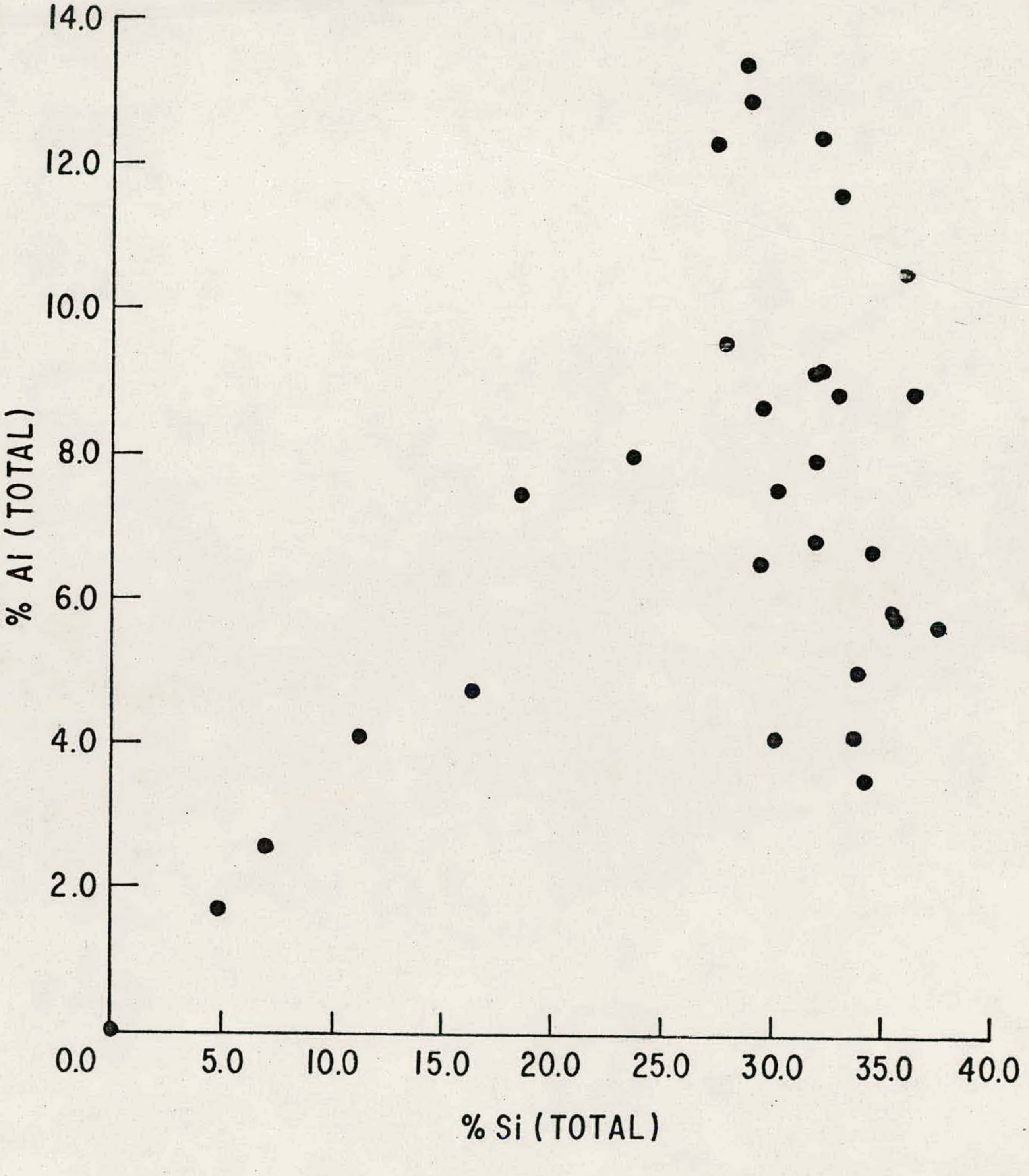


Fig 9


14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
% Al (TOTAL)
5.0
10.0
15.0
20.0
25.0
30.0
35.0
40.0
% Si (TOTAL)