Elemental Associations of Coal:

A Study of the Organic and Inorganic Association of Elements in Coal

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October 26, 1981

Abstract

Data on the associations of elements in coal are summarized from the literature. Comparison of elemental analyses by different authors illustrate numerous inconsistencies. A summary of the literature showed zirconium, lanthanum, mercury, and silver are consistently classified as inorganic in origin; arsenic, cadmium, and manganese are generally inorganic; beryllium, germanium and antimony are usually regarded as organic in origin. Inconsistencies among authors in the organic/inorganic association of elements and in the use of different analytical techniques were investigated by a random variability test to determine the reliability of the conclusions concerning the organic or inorganic preferences of the various trace elements. The results of the random variability test on data presented in the literature suggest the statistical significance of the assignment to organic versus inorganic fractions. Highly significant probabilities ($p=.001-<.0001$) were found for barium, vanadium, and silicon. The other elements tested were inconsistent and many of the random variability tests resulted in not significant probabilities ($p>.05$). Preferential sensitivity of analytical methods to detect elements in the inorganic rather than organic fraction or incomplete separation of the organic/inorganic fractions account for inconsistencies in the organic/inorganic association of elements in coal.

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Acknowledgements

The author would like to express sincere gratitude to Dr. Kuellmer for his generous guidance and assistance during the course of this study. Also, a deep sense of gratitude is felt toward Frank Kottlowski, Frank Campbell and the New Mexico Bureau of Mines and Mineral Resources for their guidance, encouragement, and financial support throughout my work. Gratitude is felt toward Dr. Martha Mitchell for her guiding questions which have directed me to important information and resources. Thank you to Dr. Renault for his advice on the thesis organization. Guidance with the statistical analyses from Dr. Gutjhar is greatly appreciated. Special thanks to Deborah Teglia for her library assistance in obtaining research articles. The author would also like to thank Keith O'Brien for editing and proofing this manuscript. Finally, the author would like to thank Rick Homans for his unending patience and dedication throughout my graduate career.

Introduction

This study presents a review of the literature on the nature, origins, and associations of the elements of coal. Furthermore, it tests the consistency of the organic/inorganic association of elements in coal from the data presented in the literature. Random variability tests were utilized to investigate the significance of data presented by nine researchers.

A large number of researchers have studied the association of elements in coal. Much of the earlier work is difficult interpret because the inorganic constituents of coal were placed into a poorly-defined category called mineral matter. Mineral matter refers to all ash-forming constituents. Recent work has shown that not all of the inorganic material present in coal are found in mineral phases (Miller, 1977). This is especially true for the low-rank coal. Since the ash-forming constituents present in low-rank coals are associated with carboxyl groups and are the result of ion exchange processes with groundwater, Miller (1977) and Given and Spackman (1978) point out that minerals and inorganics must be considered separately. The term mineral matter in the literature is more appropriately applied to the mineral and non-mineral ash-forming constituents of higher rank coal because the inorganic materials associated with higher rank coals are commonly in mineral phases.

The importance of whether an element is associated with the organic or inorganic portion of coal is four-fold. First, as pointed out by Lessing (1914) the amount of inorganic material in coal is important to industry because it affects the yield of the carbonization products as well as the structure, strength and reactivity of the resultant coke (Jenkins and Walker,1978). Inorganic constituents (mineral phases) also undergo major changes which lead to clinker formation, fly ash, slagging and boiler tube corrosion (Ely and Barnhart,1963; Borio, Henzel, Ulmer, Wilson and Leonard (1968); Watt (1968 and 1969); Mitchell and Gluskoter (1976); and Nankervis and Furlong (1980). Also important to industry and the environment are the effluent and volatile elements which can make their way up the stack. Secondly, knowledge of elemental associations in coal is important for environmental reconstruction purposes. From this data the geologist can interpret source area, conditions during deposition, secondary or post-depositional changes, and location within the basin.

Methods of Investigation

Concentrations of organically and inorganically associated elements have been studied in a number of ways with a wide variety of analytical methods. Due to differences in analytical techniques and presentation of results, no work has been done to compare conclusions of different authors. To compare the different studies, an organic fraction, inorganic fraction, and associated standard deviations were determined from the data of each researcher and each sample they studied. Where the authors did not state a standard deviation of their analytical data, acceptable values of the standard deviation were assigned according to the analytical technique used. For example, in emission spectrography, the most likely probable error is + or - 50% of the amount reported. The probable error (PE) is related to the standard deviation (s) by:

(a) $PE=0.67449s$

Data presented by each author was used in the following ways:

1) The concentration of the element in the organic (x) fraction and inorganic fraction (y) were determined. These are considered to be mean concentrations.
2) From equation (a) the standard deviation of the organic fraction (sx) and inorganic fraction (sy) were determined.
3) The difference of the means (`m$U1$D-m$U2$D`) was determined by:

(b) `x-y=m$U1$D-m$U2$D`

4) The variance (`S$D2$U`) was determined by:

(c) `S$D2$U=SQRT((sx)$D2$U+(sy)$D2$U)`

5) From the above information a corresponding Z-value for a standard normal distribution was determined by:

```
(d)       m$U1$D-m$U2$D
     Z=   ------------
             S$D2$U
```

6) Finally a probability was determined for a two-sided distribution from (Table 4 Areas Under the Normal Curve)(Walpole and Myers, pp.513, 1978).

If the probability probability was <0.0001-0.001, these numbers are considered highly significant and scored with three asterisks in the appendices. If they fall in the range 0.001-0.01 they are considered very significant and scored with two asterisks in the appendices. A probability of 0.01-0.05 is significant and scored with one asterisk in the appendices. An insignificant probability value is >0.05 and no asterick is given. These probabilities were then compared among samples of the same authors and then between authors to see what consistencies existed with regard to organic or inorganic elements in coal.

Previous Work

A number of investigators have looked at the elemental associations of coal. One of the earliest studies of the organic and inorganic associations of coal was by Goldschmidt who in 1935 investigated trace elements in coal. He identified some elements which combined inorganically in coal and also identified metal-organic complexes. He attributed vanadium, molybdenum and nickel to these metal-organic complexes. Other investigators include Horton and Aubrey (1950) Inagaki(1951); Hashimoto(1953); Zubovic, Sheffey and Stadnichenko(1960 and 1961); Finkelman and Stanton (1978);and Raymond (1979). To determine organic and inorganic affinities of various elements in coals of varying ranks, these authors analyzed the various macerals as representative of the pure coal substance. Other researchers who have studied the organic/inorganic associations of the elements of coal are Breger and Schopft (1955); Nicholls (1958); Bogdanov (1965); Razdorozhnyy(1968); Manskaya and Drozdova 1968); Szilagyi (1971) Gluskoter and Landahl (1973); Ruch, Gluskoter and Shimp (1974); Miller (1977); Gluskoter, Ruch, Miller, Cahill, Dreher and Kuhn (1977); and Kuhn, Fiene, Cahill, Gluskoter and Shimp (1980). Because this study involves a very extensive literature survey, explanations and more detailed descriptions of each author's work will be presented in the text of this paper.

Causes for the Elemental Associations in Coal

Gluskoter et al (1977) found that elements organically associated in a sub-bituminous coal from Wyoming might be inorganically associated in a coal from the Appalachians. Nicholls (1968) also noticed this trait and attributed it to the variation in age between the different seams analyzed. This seems logical since different geological events occurred at different times and brought new suites of elements into the surface geochemical systems. Observations like these raise the question of what are the factors which affect the organic and inorganic associations of the elements in coal?

Some of the factors which investigators have attributed to the many differences are: 1) source material 2) stability of the various compounds which contain metals 3) age and rank 4) environment of deposition and 5) secondary or post-depositional changes.

Source material is composed of those elements entering the basin of deposition during peat formation. At this stage the system is open and extrabasinal material is carried in either in the form of mineral phases or as soluble ions and metallo-organic complexes. This material is brought into the peat-forming environment by groundwater, meteoric waters, or by aeolian forces. Allogenic, adventitious or detrital are terms which describe these inorganic species which have been brought into the basin during peat accumulation. Another definition of adventitious material is that which can be separated from the coal substance

(Edgecombe and Manning, 1952). The soluble ions which have been brought into this depositional environment may either precipitate and form authigenic minerals or they may be assimilated by the living plants through the root system and combine organically with the plant tissues (Sprunk and O'Donell, 1942). This may occur at three stages during the coal formation. The first, which has already been mentioned occurs during the life of the plants, second, during the decay of the plants, and third, during the mineralization of the coal.

In an attempt to use plants as indicators of source material for the organically associated elements in coal, many authors have published lists of elements believed to be associated with either a particular species of plant or plants in general. Such lists may be inconclusive when based on observations of present day plants for it is not certain if the elemental composition of modern day plants is identical to ancient coal-forming plants. Miller (1931) listed ten elements necessary for the growth of all plants. They are carbon, oxygen, hydrogen, nickel, phosporous, potassium, calcium, magnesium, sulfur and iron. copper and boron, manganese and probably zinc are also believed to be essential. Kuhn, Fiene, Cahill, Gluskoter and Shimp (1980) provide a table in their report comparing the mean concentrations of elements which they predict to be organically associated and the mean concentrations of these same elements in plant material. From this comparison they have determined that the elements which are highly concentrated in plants (iron, calcium, potassium, magnesium, manganese and phosphourous) are less concentrated in the organic portion of coal. They attributed this depletion to epigenesis prior to polymerization. Casagrande and Erchull (1976), in studying the Okefenokee peat-forming environments noted that when drought occurs water levels drop. This change allows increased microbial oxidation of the organic matter and release of metals which had formed a part of the living plants. This activity may account for the depletion of metals in coal when compared to plants.

Szalay (1957) found nitrogen, phosphorous, sulfur, clorine, florine, bromine, iodine, niobium, and selenium to be elements not adsorbed by organic substances since organic matter has a negative charge and only cations will be adsorbed. These elements generally occur in their anionic form and are therefore, not absorbed.

Precipitation of authigenic minerals, plant assimilation, and organic compounds which may form, provide the stability necessary for metals to remain with the coal-forming substances throughout the coalification process. To study the associations of metals with organic materials, Zubovic (1966) says one must assume that organically associated elements "in geologically old carbonaceous materials are present in the most stable complex possible to survive through geologic time". Chelates and ring structures of metallo-organic complexes are known to be stable. Porphyrin chelates of metals are known to exist. These structures enable plant material to incorporate transition metals. For example porphyrin nuclei are structural units of chlorophyll and they retain Magnesium atoms by two ionic and two covalent bonds

(Manskaya and Drovdoza,1968). Schartz (1954) hypothesized the important role of chelate-fertilizer in the extraction of trace elements from minerals making them water soluble and available to plants. In this case, the metal ion forms the center of the complex ring structure. Zubovic, Stadnichenko, and Sheffey (1960) and Zubovic (1966) relate high ionic potential with degree of organic association. Metals with high ionic potential have high organic association in coal. Examples of metals of high ionic potential are beryllium, boron, germanium, titanium, gallium, aluminum and silicon. Zubovic (1966) states that when yttrium, gallium, lanthanum, beryllium, nickel, cobalt and zinc are bonded to organic material, they are held as chelated complexes.

Two other types of compounds can be formed by organic compounds and metals: a salt-like compound and a metallo-organic compound. The salt-like compound is formed by a metal substitution for a hydrogen of a carboxyl group. Many salts are soluble in water in a geologic sense. Metallo-organic compounds are formed when a metal bonds directly to a carbon of an organic radical (Krauskopf,1967). Martell and Calvin (1952) listed the organic compounds capable of forming internal complex compounds with metals: primary amines, secondary amines, tertiary amines, oximes, imines, thioesters, keto groups, thioketo groups, hydroxyl groups, and carboxyl groups.

The associations of elements may also be related to conditions under which the coal is being deposited. Razdorozhnyy (1968) related the irregular distribution of trace elements in coal described in the literature to changes in pH between the coal beds and country rock. For example, the Donbas Coal Beds of Russia which are 50-65 cm thick have considerable variety in pH's between each bed. He also found that coals deposited in basins with little circulation of water are alkaline and those deposited in open basins accessible to sea water are strongly oxidized. He concludes alkaline coals are better concentrators of trace elements than acid coals.

Another topic on which many researchers have concentrated is the ability to discriminate between marine vs non-marine paleo-environments. A very recent study was conducted by Bailey (1981) who studied the differences between coals formed in marine-influenced and fluvial paleo-environments of the Lower Kittanning Coals. He concluded that fluvial samples are higher in copper, chromium, titanium, potassium, silicon, and aluminum, while marine-influenced samples are more concentrated in zinc, iron, pyritic sulfur and sulfate sulfur.

Variations in age and rank account for the differences in elemental associations. Lower rank coals differ from coals of higher rank in that they have higher oxygen contents. This oxygen is in the form of weakly acidic and reactive functional groups (Van Krevelan,1961). The functional groups are involved in ion-exchange and chelation with metals. Lower rank coals are also known to have some humic acid present which serves as progenitors for coals of higher rank (Breger,1955). Humic acids, though they are not contained in plants play an important role in the formation of the organic portion of peats and are capable of combining with certain elements. Uranium, vanadium, gallium, molybdenum, nickel, and copper are examples of elements which are able to do this (Manskaya and Drovdoza,1968). Manskaya and Drovdoza (1968) stressed the role of humic acids in mobilizing and trapping metal cations.

Behavior of elements associated with coal post-depositionally and the diagenetic changes which take place is not well understood. As rank increases there is a decrease in porosity , moisture content, and optical anisotropy increases (Stach, 1975). As the porosity amd moisture content decreases so does the ability for extrabasinal material to enter the coal except through fractures. Miller (1977), who studied the lignites from South Dakota, found elements that are organically associated in bituminous coals to be associated in the same way in lignites, but with the total content of a number of elements in lignite being greater than bituminous coal.

Published Data on the Elements in Coal

Brief descriptions of published work of a number of researchers who have investigated organic and inorganic associations of elements in coal is included. Analytical techniques, precision, type of coal analyzed and the results of the authors are summarized in Table 1.

Bogdanov (1965) collected over 15,000 samples of Russian bituminous coals, coal inclusions in country rocks, and country rocks for semiquantitative spectral analysis. From these analyses he grouped the elements into three catagories: those which form insoluble metallo-organic compounds with humic acids and are closely related to organic substances: Ge, Tl, Sc, Cd, Mo, Sb, As, P, Pb, Zn; elements associated with terrigenous material are Ti, Cr, Zr, Au, Y, Ce, La, W, Sn, Ni, and Ag; and the final group is variable in association: Fe, V, Cu, Ba, Sr, and Mn.

Breger, Duel and Rubenstein (1955) analyzed spectrographically a sample of lignite from the Mendenhill strip mine, Harding County, South Dakota. From their work they suggest that uranium is present in the organic portion of the coal and is held in the coal as an organo-uranium compound. Also, Ni, Co, Be, Mo, Ti, V, Cr and Sn are present in the demineralized lignite.

Dalton and Pringle (1962) studied the content of gallium in the Warwickshire Coalfield, Cannock Chase, Shropshire and North and South Staffordshire Seams, England. Associated roof and floor samples were also analyzed. Spectrographic analyses were conducted to determine concentrations. As a result of this investigation, it was determined that gallium is variable in association and is present in the finely divided alumino-silicates intimately mixed with the coal. A small quantity was associated with the organic and inherent mineral matter of the coal.

Duck and Himus (1952) studied the mode of occurence of arsenic in commercial coal and coke samples. Age, rank, and names of the seams sampled have not been given in the article. Arsenic was determined by a modified Gutzeit Process on the coal as received and retained in the coal ash. They concluded that arsenic occurs in the coal as arsenopyrite and to some extent as an oxidation product of arsenopyrite.

Gluskoter and Lindahl (1973) studied the cadmium contents of twenty-three Illinois Coals. They hypothesized from their work that cadmium substitutes for zinc in sphalerite and in coal it is asssociated with the high specific gravity fraction or sink.

Gluskoter, Ruch, Miller, Cahill, Dreher, and Kuhn (1977) analyzed 172 whole coal samples, 40 of which were bench samples and 64 were washed coal samples. 114 of the samples were from the Illinois Basin. Five of the nine washed coal samples were also from the Illinois Basin. The other samples are from other areas in the United States. Ions were determined using a number of analytical techniques. In table J of their text is a summary of the techniques used for each element. From the washability studies they determined an index of organic affinity for the elements and catagorized them as: 1) organic 2) intermediate-organic 3) intermediate-inorganic and 4) inorganic. They concluded that Ge, Be, B, and Sb were organically associated and Zn, Cd, Mn, As, Mo, Fe and inorganic.

Horton and Aubrey (1950) studied the distribution of minor elements in three samples of vitrain of different ranks from the Barnsley Seam of South Yorkshire, England. The samples were taken at 12 mile intervals. The vitrains were hand separated from the coal and ground so that they passed through a 100 Bs test-sieve. Microscopic examination followed to determine how pure the vitrains were. Thurcroft and Markham Main were found to be of high purity. Because a number of fusain bands were present in the Dalton Main Sample it was impossible to isolate the vitrains by hand. Horton and Aubrey (1950) then used float-sink separation methods. The different density fractions were then ashed and examined with a quartz spectrograph to determine the following minor elemental concentrations: Sb, Be, B, Cr, Co, Cu, Ga, Ge, Pb, Mn, Mo, Ni, P, Sn, Ti, V, Zn, and Zr. The coal was ashed at 400 degrees centigrade. The quantities of the elements present were estimated by a visual comparison of intensities of the samples as compared to a series of standards.

Based on graphic representation of the ideal variation in concentration for elements associated with 1)the organic portion (pure coal substance) 2)the inorganic portion (adventitious) and 3) variable association, Horton and Aubrey (1950) grouped the elements according to varying proportions contributed by each fraction. A scoring system was then created in which a value of one means that all of the element is contributed by the pure coal substance; 3/4 implies that 3/4 of the element is contributed by the pure coal substance and 1/4 was contributed by the adventitious material. They determined that the number of elements interpreted to be associated with the organic or pure coal substance are variable between vitrains from the same seam. Although some generalities may be determined, Be, B, Ga, Ge, Ti and V all seem associated with the pure coal substance while, with the exception of Cu, none of the elements examined show evidence for association with the adventitious portion of the coal.

Inagaki (1968) made colorimetric determinations of Ga and Ge in Japanese lignites and coals. He found that Ge may be more firmly retained in lignites than in coals. He also found that Ga is associated with the adventitious mineral matter.

The work of Kuhn, Fiene, Cahill, Gluskoter and Shimp (1980) includes data from the studies by Gluskoter et al (1977), Kuhn et al (1978) and Kuhn, Fiene and Harvey (1978). In the 1980 study by Kuhn et al (1980), 27 coals from the various regions of the United States-Eastern, Central, and Western-were investigated. The samples were subjected to gravity separations and chemical demineralization in order to achieve a more complete separation of the organic and mineral fractions of the coal since gravity separation "seldom if ever, results in a complete separation of mineral matter from the coal" (Kuhn et al, 1980). Elemental concentrations were then determined using a number of analytical techniques. These include: neutron activation, X-ray fluorescence, wavelength-dispersive, direct-reading optical emission spectroscopy, prompt gamma-ray/neutron activation and X-ray fluorescence-energy dispersive. For the Illinois Coals: Br, Ge, Be, Sb, B, and organic Sulfur were found in the organic phase. Zn, As, Cd, Fe, and pyritic sulfur were consistently associated with the inorganic material. Zr, Hg, Pb, Hf and Mn were found to be inorganically associated and easiliy removed. Al, Si, Ti, Mo, K, P, Ga, Ca, Cr, Co, Ni, Cu, Mg and Se were variable in association.

Miller (1977) studied the geochemistry of lignites from South Dakota in his doctoral dissertation. His work indicates that Ca, Na, K, Sr, Ba, Mg, and Mn are present in an ion-exchangable form attached to organic acid groups. Chelated organic complexes contain Al, Ti, Be, and V. These chelated organo-metallic complexes are decomposable in dilute mineral acid. Because these cations are associated with carbonates as well this catagory is considered variable in association. Another group Si, Al, K, Mg, Zr, and Ti are present as detrital minerals. Miller concluded that "a surprisingly large number of elements in lignite owe their association to interactions with organic matter, and that the organic matter has had a profound influence in determining the distribution of many elements in the seam".

Nicholls (1968) compared a number of coal analyses and plotted the concentrations of various elements in coals against the ash content of the coal. Diagrams were presented depicting a number of such points for a single coal seam or group of coal seams in a single geographic area. These points were then interpreted for degree of inorganic and organic association of elements. The seams used in the analysis were the Svea Seam, Spitzbergen (Butler, 1953), the Lloyd Cove Seam, Nova Scotia (Hawley, 1955), and the New South Wales Coalfield (Swaine, 1962). These seams differ in age. For example, the Svea Seam is of Cretaceous age and the Lloyd Cove Seam is of Upper Carboniferous age. Nicholls described elements as: associated with the organic portion; associated with the inorganic portion; variably associated; high concentration of element and associated with the inorganic portion; and high concentration of the element and associated with the organic portion of the coal. Nicholls (1968) determined B to be inorganically associated and Pb, Co, Cr, Ba, Sr and V to be inorganically associated. Ge, Ga, Ni, Mo, As, and Cu he found to be variable between the different seams. Ni and Cu were inorganically associated when their concentrations in the coal were high. This was also true of Ga and Ge which were organically associated when their concentrations were high in the coals. Nicholls accounts for the variability of some of the elements studied due to the differences in age of the different seams.

Razdorozhnyy (1968) studied the acidity of bituminous coals from the Bagansk area of the Donbas, U.S.S.R. and attempted to correlate fifteen elements with pH values and ash contents. A set of coal and enclosing rock samples (argillite and siltstone) were analyzed using heavy liquid separations. From his investigation, he found that Co, Ni and Be are found in the organic fraction, while Pb, V, Sn, Cr, and Ag are found in the inorganic portion of the coals. Zn, Ga, Sc, Cu, Yb, Y and Mo are variable in association.

Ruch, Gluskoter and Shimp (1974) have determined elemental concentrations for 21 elements on four samples of coals from the Illinois Basin (Illinois, Indiana, and Western Kentucky). The seams studied include the Davis Member and the Dekoven Member of the Matton Formation, Colchester (No.2) and Herrin (No.6). From gravity separations, they determined an organic affinity index. Elemental concentrations were determined using a variety of analytical techniques including x-ray fluorescence, optical emission spectrometry, atomic absorption, neutron activation and ion-selective electrode analysis. From their data, they found that Ge, Be, and B have the greatest organic affinities and tended to be concentrated in the clean coal fractions. Hg, Zr, Zn, Cd, As, Pb, Mn, and Mo were concentrated in the mineral matter portion of the coal and have the least organic affinity. They found P, Ga, Ti, Sb and V to be variably associated but more closely allied to the elements with high organic affinities. A fourth group was identified as being variable, but as more closely related to the elements with inorganic associations. These elements are: Co, Ni, Cr, Se and Cu.

Szilagyi (1971) also used spectrographic methods to determine the association of Mo, V, and Cr in coal samples from Hungary. A portion of his work includes the data of Szava (1966 and 1967) from two coal beds. The Mecsek Coals are of Liassic age (Lower Jurassic) and the Borsod Coals are Miocene. The Mecsek

Coals have high concentrations of Mo and the Borsod Coals are V and Cr-rich. The seams were sampled in intervals. The units of these intervals were not indicated. It is important to note that the sampling also included the carbonaceous shales between the coal layers as well as the shaly layers above and below the coal units. An ideal diagram of the expected relation between the metal concentration in the ash and organic material was determined. As a result of his analysis, Szilagyi found Mo to be organically associated. When Mo is found in low ash coals it is in higher concentrations than would be expected just from the accumulation of ash and organic plant material. Szilagyi attributed this to secondary Mo enrichment through the groundwater. Cr and V were not so clear cut in their distribution and are interpreted to be variably associated.

Valeska, Malan and Kessler(1967) studied trace elements of the Ostravakarvina Coal District of Czechoslovakia and determined that Ge, Be, P, B and V increase with decreasing ash and are associated with what they call the "inner ash" of the organic matter. Analytical methods used were not indicated.

Thallium in coal has been studied by Voskresenskaya (1968). He has established through quantitative spectographic analyses that thallium in a number of coal basins in the Soviet Union accumulates in sulfide inclusions, especially in pyrite and is therefore inorganically associated.

Zubovic, Sheffey and Stadnichenko (1960, 1961, and 1964) and Zubovic (1966, 1976) also studied the organic/inorganic association of elements in coal. Their analyses were conducted in a manner similar to Horton and Aubrey (1950). Thirteen samples of coal were separated into float-sink fractions; two samples were separated into five fractions, and the third sample into three fractions. The samples originated from several different beds, the Minshall Seam, Indiana (member of the Tradewater Group), and Number 9, and Number 5, Kentucky (both members of the Carbondale Group). A diagram was used to present their data as those elements which are asssociated with the float and those associated with the sink. From this information, Zubovic et al (1960, 1961, and 1964) made a list of elements in order of decreasing association with organic matter: Ge, Ga, V, Be, Ti, B, Ni, Cr, Co, Y, Mo, Cu, Sn, Zn and La. The first six: Ge, Ga, V, Be, Ti and B are identical to the results of Horton and Aubrey (1950). Zubovic (1966) added that this series is related to the chelating properties of the metals. Table 1 is a summary of the various authors, analytical methods used, location of coal sampled, age, and rank of coal.

Table 1:

Summary of Authors

Author	Analytical Method	Geographic Location	Rank & Age
Bogdanov (1965)	Spectral Methods	Russian Coal	
Breger, Duel and Rubenstein (1955)	Spectrographic Analysis Chemical extraction in 1 N HCl acid	Mendenhill, South Dakota	Lignite age not indicated
Dalton and Pringle (1962)	Spectral Methods Carbon tetrachloride and Carbon tetrachloride-benzene mix 1.32,1.40,1.59	Warwickshire, Cannock Chase, Shropshire, North and South Staffordshire	Bituminous age not indicated
Duck and Himus (1952)	Gutzeit Process		Bituminous Coal and Coke age not indicated
Eskenazy (1977)			
Gluskoter and Lindahl (1973)	Atomic Absorption Spectrophotometry	Illinois Coal	Bituminous Carboniferous
Gluskoter, Ruch, Miller, Cahill, Dreher and Kuhn (1977)	Atomic Absorption X-ray Fluorescence Neutron Activation Emmision Spectroscopy	Illinois Basin U.S. Coals	Bituminous Carboniferous
Horton and Aubrey (1950)	Spectral Methods	South Yorkshire Coals	Vitrains of various unspecified ranks

Table 1:
(Continued)
Summary of Authors

Author	Analytical Method	Geographic Location	Rank & Age
Inagaki (1968)	Colorimetric Analysis	Japanese Coals	Lignites and Coal of various unspecified rank
Kuhn, Fiene, Cahill, Gluskoter and Shimp (1980)	Atomic Absorption X-ray Fluorescence Neutron Activation Emmision Spectroscopy	Illinois Coals	Various unspecified ranks
Manskaya and Drozdova (1968)	Dilute alkali solution		Peat age not indicated
Miller (1977) and Miller and Given (1978)			Lignite age not indicated
Nicholls (1968)	Graphic Interpretation	Lloyd Cove, Nova Scotia Svea, Spitzbergen	Bituminous Pennsylvanian
Otte (1953)			
Razdorozhnyy (1968)			
Ruch, Gluskoter and Shimp (1974)	Atomic Absorption Optical Emmision Spectroscopy Neutron Activation X-ray Fluorescence Ion-Selective Electrode	Illinois Coals	Bituminous Carboniferous

Table 1:
(Continued)
Summary of Authors

Author	Analytical Method	Geographic Location	Rank & Age
Szilagyi (1971)	Spectrographic Methods	Hungarian Coals	Unspecified rank Miocene
Valeska, Malan and Kessler (1967)		Ostava-Karvina, Czechoslovakia	
Voskresenskaya (1968)	Quantitative Spectrography	Middle Asia; Donbas Basin, Karaganda and Moscow Coal Fields, Dnepr Basin, Transcarpathian Region, U.S.S.R.	Unspecified rank Jurassic Paleogene Neogene
Zubovic, Sheffey and Stadnichenko (1960, 1961 and 1964) Zubovic (1966 and 1976).		Eastern Interior, U.S.A. Coals	

Table 2 provides a summary of the work previously discussed on elemental associations of coals. The various elements have been categorized as either organic, inorganic, or variable in their associations with coal. Other workers listed in Table 2 such as Manskaya and Drovdoza (1968) Otte (1953) and Eskenazy (1977) were added out of interest because they have studied mechanisms by which elements are combined with the organic fraction rather than determining with which fraction the elements are associated.

Associations of elements in coal are inconsistent. This may be due to a number of factors, many of which have already been mentioned: age, rank, source material, differences in diagenesis, secondary contamination by marine waters, differences in acidity of the coal, location within the basin of deposition, and differences in analytical technique.

Table 2:

Summary of Organic and Inorganic Associations in Coal.

AUTHOR	ORGANIC ASSOCIATION	INORGANIC ASSOCIATION	VARIABLE ASSOCIATION
Bogdanov (1965)	Ge,Tl,Sc, Cd,Mo,Sb, As,P,Pb, Zn.	Be,Ti,Cr, Zr,Au,Y, Ce,La,W, Sn,Ni,Ag.	Fe,V,Cu, Ba,Sr,Mn.
Breger, Duel and Rubenstein (1955)	U,Ni,Co, Be,Mo,Ti, V,Cr,Sn.		
Dalton and Pringle (1962)			Ga
Duck and Himus (1952)		As	
Eskenazy (1977)		W	
Gluskoter and Lindahl (1973)		Cd	
Gluskoter, Ruch, Miller, Cahill, Dreher and Kuhn (1977)	Ge,Be,B, Sb	Sn,Cd,Mn, As,Mo,Fe	Co,Ni,Cu, Cr,Se
Horton and Aubrey (1950)	Be,B,Ge, Ti,V	P,Mn,Sn	
Inagaki (1968)	Ge	Ga	

Table 2:
(Continued)
Summary of Organic and Inorganic Associations in Coal.

AUTHOR	ORGANIC ASSOCIATION	INORGANIC ASSOCIATION	VARIABLE ASSOCIATION
Kuhn, Fiene Cahill, Gluskoter, and Shimp (1980)	Br,Ge,Be,B Sb	Zn,As,Cd, Fe	Ti,Al,Ca Ga,Ni,P, Si
Manskaya and Drozdova (1968)	Ge		
Miller (1977) and Miller and Given (1978)	Na,K,Ca, Mg,Sr,Mn	Mo,Si,Al, K,Mg,Zr	Al,Ti,Be, V
Nicholls (1968)	B	Pb,Cr,Co, Ba,Sr,V	Ga,Ge,Ni, Mo,Cu
Otte (1953)	Be		
Razdorozhnyy (1968)	Ni,Co,Be.	Pb,V,Sn, Cr,Ag.	Zn,Ga,Sc, Cu,Yb,Y, Mo.
Ruch, Gluskoter, and Shimp (1974)	Ge,Be,B.	Hg,Zr,Zn, Cd,As,Pb, Mn,Mo.	P,Ga,Ti, Sb,V,Co, Ni,Cr,Se, Cu.
Szilagyi (1971)	Mo.		Cr,V.
Valeska, Malan, Kessler (1967)	Ge,Be,P, Be,V.		
Voskresenskaya (1968)		Tl	
Zubovic, Sheffey, and Stadnichenko (1960,1961 and 1964). Zubovic (1966 and 1976).	Ge,Be,Ga,B Ti,V, Ni,Cr,Co,	Zn,Sn La.	

From Table 2, it can be seen that Ge shows the greatest consistency in its association with the organic fraction of the coal. Only Nicholls (1968) believes Ge to be variable in its association. There is also agreement among Bogdanov (1965) and Zubovic et al (1960, 1961, 1964, 1966 and 1976) that Lanthanum is inorganic in its association. Bogdanov (1965) and Ruch et al (1974) place zirconium in the inorganic portion of the coal. Silver according to Bogdanov (1965) and Razdorozhnyy (1968) is inorganic. Tungsten is inorganic in its association (Bogdanov (1965) and Eskenazy (1977)). Mercury according to Ruch et al (1974) is inorganic. Gluskoter and Lindahl (1973), Kuhn et al (1980), Ruch et al (1974), and Gluskoter et al (1977) agree that cadmium is inorganic in association. Bogdanov's (1965) data is in disagreement. He concludes that cadmium is organic. Duck and Himus (1952), Gluskoter et al (1977), Kuhn et al (1980) and Ruch et al (1974) have all stated that arsenic is found in the inorganic portion of the coal. Bogdanov's (1965) results are different. According to him arsenic is organically associated. Lead, it is agreed, is inorganically associated by all the authors with the exception of Bogdanov. He has concluded that lead is organic. Manganese is also inorganically associated with the exception of Bogdanov who found it to be variable in association, and Miller (1977) and Miller and Given (1978) who found manganese to be organic.

All of the authors listed who have studied boron agree that it is organically associated. Vanadium is also organic in its association (Breger et al (1955), Horton and Aubrey (1950),Valeska, Malan and Kessler (1967) and Zubovic et al (1960, 1961, 1964, 1966 and 1976)). Bogdanov (1965) found vanadium to be variable. Nicholls (1968) and Razdorozhnyy (1968) consider vanadium to be inorganically associated. Antimony is organic with the exception of Ruch et al (1974) who found antimony to be variable. Beryllium is organic according to most of the researchers except Bogdanov who believes it to be inorganic and Miller (1977) and Miller and Given (1978) who believe beryllium to be variable.

The other elements do not fall consistently into one category or another. For example, molybdenum is considered to be organic by Bogdanov (1965), Breger et al (1955), and Szilagyi (1971). Ruch et al (1974) and Gluskoter et al (1977) have found molybdenum to be inorganically associated. Kuhn et al (1980), Nicholls (1968), and Rasdorozhnyy (1968) have concluded that molybdenum is variable in association. Phosphorous, titanium, zinc, chromium, lead, vanadium, magnesium, tin, nickel, strontium, thallium, barium, and gallium are other examples of elements which are inconsistent in their associations.

From this information, the following summary can be made. Zr, La, Hg and Ag are consistently inorganically associated while Be, Ge, Sb and V are largely organically associated on the basis of data of all workers with no more than one exception. Boron is considered by all of the authors listed to be organic. There is agreement that As, Cd, and Mn are inorganically associated except for one author. Because of the disagreement between many researchers a random variability test has been used to verify the extent to which the elemental associations are different. The random variability test determines the probability that the data represent two differing groups.

Statistical Analysis

The major difficulty when studying elemental associations is obtaining statistically valid samples. This is difficult because of the inability to completely separate the inorganic material from the organic material. Specific gravity techniques have been most widely used to separate the organic and inorganic fractions and is presently used by industry during coal cleaning. The specific gravity technique assumes that the organic portion has a low specific gravity, (<1.30), whereas density fractions more than 1.60 are largely mineral matter. This technique can separate the sample into some portions which are mineral rich and others which contain relatively pure coal, but separation is incomplete (Ruch, Gluskoter and Shimp (1981). Important in maximizing release of intimately associated minerals from the organic matter is the grain size of the coal. Fractionation of finely-ground coal is preferred to coarsely-ground coal (Miller, 1977).

Most of the authors studied have used specific gravity separations to divide the organic from the inorganic portion of the coal. Once the two fractions are separated, the authors determined the elemental concentrations by differing methods.

This difference in analysis produces differing precision so that a statistical analysis is necessary to compare the results of the various authors. A common statistical test has been used which compares the differences in concentration of an element between the organic and inorganic fractions and determines the likelihood is due to random selection of sample.

A number of assumptions have been made so that standard deviations, differences between means, variance of means, and probabilities could be determined. The following is a description of these assumptions for each publication used. The results of these statistical tests are presented in the Appendix of this text. This section will be followed by a series of tables which will provide a summary by element of the results of the tests on the published data.

Breger, Duel and Rubenstein's (1955) associations of elements in ashed float-sink separates were presented in the following ranges of percent: >10%, 10-1%, 1-0.1%,0.1-0.01%, 0.01-0.001%, and 0.001-0.0001%. Since they used semi-quantitative spectrographic analyses for the elements studied, a value of 3.2 was used because 3.2 is the geometric midpoint value between 1 to 10 on a logarithmic scale. Likewise, 0.32 was used for the 1 to 0.1 range, etc. Because emission spectrographic methods were used, + or - 50% was considered to be the probable error as was determined by Horton and Aubrey (1950).

The statistical test described on page 3 of this text was then used to determine the reliability of the elemental associations. Appendix 1 presents the results of Breger et al (1955).

Kuhn et al (1980) in their study of Illinois, Eastern and Western Coals have listed in their text (table 7 on page 31) the mean concentrations and retention percentages in mineral-matter-free coals. To apply the statistical test to Kuhn et al's (1980) numbers, mineral-matter-free numbers were assumed to be the organic fraction, the raw coal minus the mineral-matter-free portion is considered inorganic. The error term for the organically associated elements are the probable error terms of the mineral-matter-free numbers. The probable error term for the inorganic portion is the sum of the errors of the two fractions.

Appendix 2 shows the results of these tests.

Ruch, Gluskoter and Shimp (1974) present the concentration of trace elements in the various specific gravity fractions in their text (table 10 on page 31). The 1.28 gravity fraction was considered organic and >1.60 was considered inorganic for the Davis Seam. In the DeKoven Seam 1.29 and >1.60 are organic and inorganic, respectively. In Colchester #2 and Herrin #6, 1.25 is organic and >1.60 is inorganic. Standard deviations for each of the elements studied were given in their text (table 6, page 19). Numbers are treated as described on page 3 of this text. The probabilities determined are shown in Appendix 3.

Appendix 4 shows the probabilities determined from the work of Horton and Aubrey (1950). Fraction #1 is considered organic and 4 is inorganic. These numbers were then treated as described on page 3.

The numbers from Dalton and Pringle's (1962) article (table 1, page 44 of their text) show gallium in ppm coal to be organic and gallium in the ash as inorganic. Because they use spectrographic methods to obtain the concentrations of the element, a plus or minus 50 percent value is assumed to be the probable error term and a similar statistical treatment was used Appendix 5 presents the results.

Szilagyi (1971), who studied Mo, Cr, and V, presents his data in his text (table 1, page 1076). The parts per million (ppm) value of the elements in the coal and ash represent the organic and inorganic fractions, respectively. It is also assumed that because spectrographic data is presented plus or minus 50 percent represents the error value and the numbers have been treated similarly to Horton and Aubrey. Appendix 6 presents the results.

Duck and Himus (1952) studied arsenic using specific gravity methods (table 1, page 268; and tables 4 and 5, on page 270) on coal and coke samples. It was first necessary to convert As$U2$DO$U3$D values ppm to As ppm. In table 1, of their text arsenic in coal is assumed to be the organically associated arsenic while arsenic in the ash is inorganic. The error term is considered to be from 4 to 10 percent as stated by the author. The largest error, 10 percent, was used to determine the standard deviations. In tables 4 and 5 of their text for two of the samples float-sink tests are shown. B12 and L1. 1.283 is assumed to be the organic fraction and 1.517 the inorganic portion in B12. 1.374 is considered organic and 1.519 inorganic in L1. All of the data were treated similarly to the above mentioned authors. Appendix 7 presents the results.

Zubovic et al (1960) present their data graphically. In order to determine numerical values for the organic and inorganic fractions, it was necessary to measure the concentrations from figure 41.1, (page B85) of their text representing percent recovered from float and sink. They state in their text that a procedure similar to Horton and Aubrey (1950) which implies spectographic methods were used. Therefore, the probable error was assumed similar, plus or minus 50 percent, and the data was treated in the same fashion as described on page 3. Appendix 8 presents the probabilities determined.

Miller (1977) presented his data in the appendix of his thesis. The numbers are presented as ppm values for different specific gravity fractions. He has also catagorized the various concentrations by type of chemical fraction. To determine probabilities on these numbers similar elements of each different treatment were added together for the float of the <1.40 liquid and the sink fraction of the >1.80 liquid. Standard deviations were determined from the precision of the techniques used. For the elements determined by atomic absorption a value of 5 percent (Lynn Branvold, personal communication) was used for Ca, Mg, Na, K, S, Ba, Mn, Ti, Al, Cu, Zn, and Fe. Emission spectroscopy was used by Miller to determine Cr, Yb, Ni, V, beryllium, Zr, Ce and La, so that plus or minus 50 percent was used as a probable error for the statistical analysis in the same manner as used for Horton and Aubrey (1950). Appendix 9 presents the results.

Several of the researchers presented in Table 2 could not be treated statistically such as Inagaki (1968) because his work was unobtainable at the time of this study. Razdorozhnyy's (1968) work was not tested because his data are presented as correlation coefficients. Gluskoter et al (1977) data were used in the Ruch et al (1980) article so a statistical analysis of both would be redundant. Voskresenskaya (1968) was also not used in this analysis. His data are presented in ranges which are to large to assume an average value. Eskenazy (1977) was added to Table 2 to provide a consensus of the relationship of tungsten to coal. His article does not present analytical data in a form which could be used. Gluskoter and Lindahl (1973) also did not present their data in a manner conducive to its use in this paper.

Tables 3 through 29 show the probability of the elements studied by the various authors may be classified as organic or inorganic on the basis of a significant enrichment in either the organic or inorganic fraction. The tables have been divided into organic and inorganic based on the abundance in each fraction. If the numbers were larger in one fraction than the other, for example the organic fraction, a star is placed in the organic side of the graph. All of the stars in the graphs represent one sample with the exception of Dalton and Pringle (1962), Szilagyi (1971) and Duck and Himus (1952) whose stars represent an average of the probabilities of the samples studied.

From these tables the probability that an element may be assignied either to an organic or inorganic fraction shows wide scatter. analyses can be seen. Aluminum was not classified in Table 2 but is known to occur in coal as allogenic and authigenic clay minerals. Because of its association with mineral matter, aluminum is expected to be found in the inorganic fraction. This is the case for Kuhn et al (1980) and Ruch et al (1974) but not for Miller (1977) and Breger et al (1955) in Table 3. The statistical test for Miller (1977) has determined that his numbers are highly significant and are more highly concentrated in the organic fraction. Miller and Given (1978) note that the amount of aluminum in the acid soluble fraction is higher in the float than in the sink and that the rest of the aluminum is in acid insoluble form. From this they infer that some of the aluminum is chelated to organic matter.

Figure 1 shows the probability of aluminum in the organic and inorganic fractions plotted against concentration. Both the highly significant inorganic and highly significant organic portions of the graph have been divided in the same format as Table 3. The tick marks indicate highly significant, very significant an significant values. The tick marks in the not significant region indicates the seperation of inorganic and organic not significant probability region. Note that in Figure 1 the high concentrations of aluminum are associated with in inorganic fraction, whereas the low concentration is associated with the organics.

The results in Table 4 of the tests of arsenic are more consistent. Both Ruch et al (1974) and Duck et al (1952) have highly significant probabilities indicating arsenic in the inorganic fraction is not due to random selection of a homogeneous population. These results are in agreement with the predictions of the authors summarized in Table 2. Arsenic is generally associated with sulfide minerals and is probably in solid solution with minerals such as pyrite and marcasite (Gluskoter et al, 1977). This is consistent with the results in Table 4. The arsenic values shown in figure 2 also show that low concentrations of arsenic are associated with the inorganic fraction.

Table 3

Aluminum

Organic Not Significant Inorganic

p<.0001	.001	.01	.05	1.0	.05	.01	.001 <.0001	
				**	*			Kuhn et al (1980)
				**			**	Ruch et al (1974)
*								Miller (1977)
			*					Breger et al (1955)

Table 4

Arsenic

Organic Not Significant Inorganic

p<.0001	.001	.01	.05	1.0	.05	.01	.001 <.0001	
				*				Kuhn et al (1980)
				*	**		*	Ruch et al (1974)
							*	Duck et al (1952)

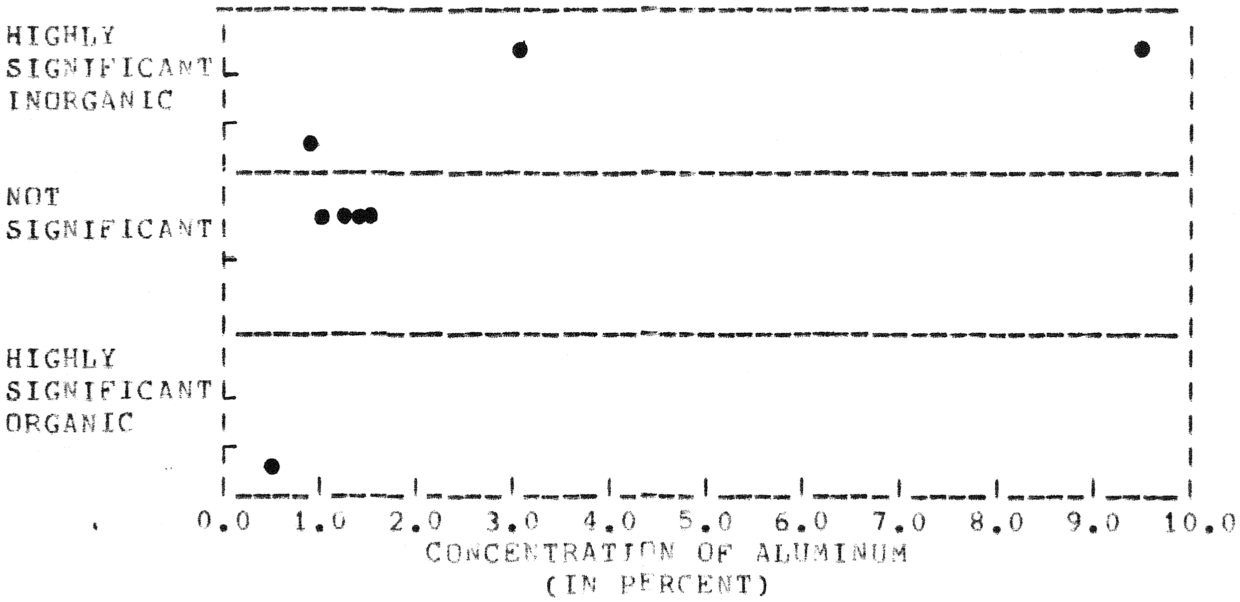

FIGURE 1

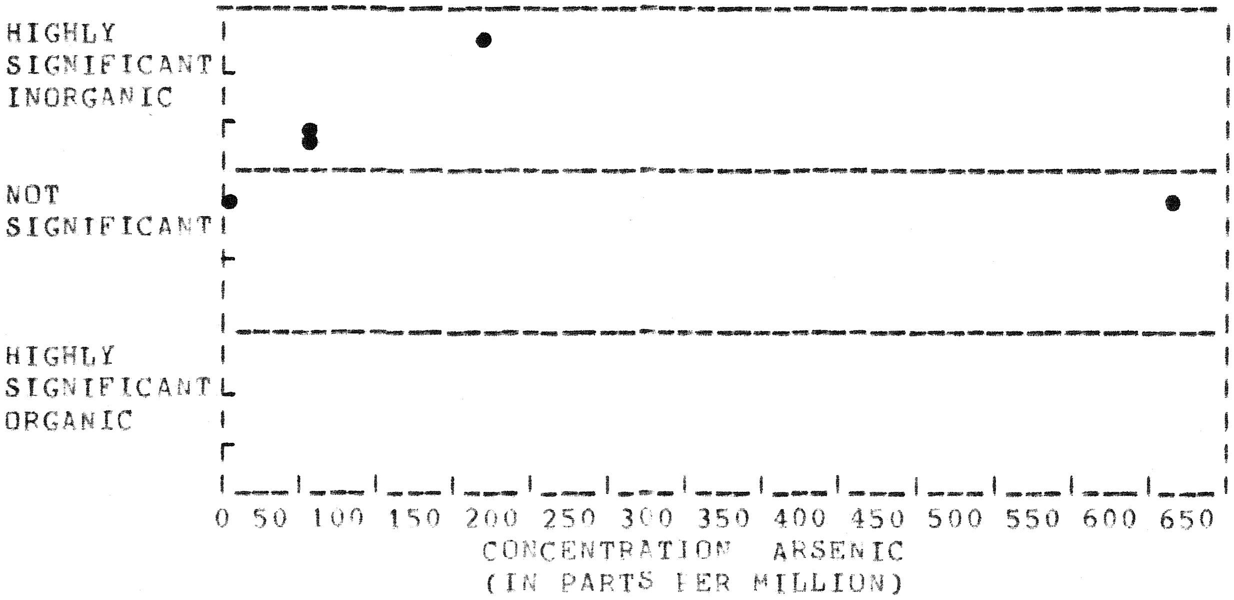

FIGURE 2

Boron, considered to be organically associated according to Table 2, displays no such distribution in Table 5. Only one of the samples of Kuhn et al (1980) shows a significant difference in the concentration of boron in the organic and inorganic fractions. Boron is suggested by Couch (1971) and Bohor and Gluskoter (1973) to be an indicator of paleosalinity. High concentrations (300 ppm) of boron (Fredrickson and Reynolds, 1960) indicate normal marine salinities. The difference in salinities may be the cause for the lack discrimination between organically and inorganically associated boron. Gluskoter et al (1977) found that boron is more highly concentrated in coal samples from the Illinois Basin Coal than from the Eastern and Western United States. This can be seen in Table 5. The work of Kuhn et al (1974) which was originally presented in Gluskoter et al (1977) shows the Herrin #6 sample to be highly significant while the other values are not significant and represent samples from the Eastern and Western United States. According to the work of Kuhn et al (1980), boron is highly significant and inorganically associated. Figure 3 shows no specific distribution for boron throughout the various concentration ranges. The probabilities are not significant and random selection was a factor in this elements distribution.

In Table 2 barium has been summarized as one of the elements which has an unclear association, possibly due to its ion-exchange character and similarity to calcium (Miller and Given, 1978). In Table 6, barium is consistently inorganically associated with a high likelihood. Barium is also inorganic at various concentrations in figure 4.

Magnesium, strontium, manganese, sodium, and potassium are all predicted by Miller and Given (1978) to be in an ion-exchangeable form in low-rank coals. Elements that are organically associated in bituminous coals are associated in the same way as in lignites, but with greater ammounts of total content in lignites than in bituminous coal (Miller, 1977). This indicates that these elements are comparable between different ranks. Magnesium and strontium have inconsistent associations as indicated in Table 2. Manganese is more consistently regarded as inorganic with the exception of Bogdanov (1965) who considers manganese to be variable in its association. In Table 2 the authors do not list sodium and potassium except in 2 cases. Miller (1977) summarizes sodium as organic and Kuhn et al (1980) concludes that sodium is variable in association. Tables 7, 8, 9, 10, and 11 show the random variability tests for these elements. Both magnesium and strontium are inconsistent in their associations and in agreement with the predictions in Table 2. Magnesium and strontium probabilities are plottd against their concentration in figures 5 and 6. a low concentrations magnesium has no distinct distribution. From one analysis, strontium is shown to be organic in figure 6.

Magnesium shows highly significant probabilities for both organic and inorganic association. Manganese is consistently inorganic with several probabilities which are highly significant as predicted in Table 2. In figure 7, manganese is inorganic at low concentration ranges.

Sodium is inconsistent in Table 10. Only Miller's (1977) numbers are highly significantly organic. The data of Kuhn et al (1980) and Ruch et al (1974) have a marginal likelihood that they may be the result of enrichment in the inorganic fraction. Sodium, based on its probability versus concentration plot, shows a variable distribution between the organic and inorganic fractions (figure 8). Potassium, in figure 9, iis inorganic throughout the entire concentration range.

The inconsistencies of magnesium, manganese, sodium, and potassium are likely to be related to the variable associations of these elements prior to coal deposition. Magnesium, manganese, sodium, and potassium are considered by Miller (1931) to be elements necessary for the growth of all plants. It is also known that MgO is always present in kaolinite and K$U2$DO and Na$U2$DO are often present in kaolinite (Weaver and Pollard, 1975). Magnesium substitutes for aluminum in the octahedral sheets of smectites (Grim, 1968). Also, MgO, Na$U2$DO, and K$U2$DO have also been identified in montmorillonite samples (Grim and Kulbicki, 1961). Magnesium may substitute for calcium in the calcite lattice and form dolomite. Manganese may substitute for iron in pyrite from a variety of different environments (Maclean and Shimazake, 1976; Raiswell and Plant, 1980; Keith and Degens, 1959; and Mitchell, 1968).

Table 5

Boron

Organic			Not Significant				Inorganic	
p<.0001	.001	.01	.05	1.0	.05	.01	.001 <.0001	
				**			*	Kuhn et al (1980)
			**	*				Ruch et al (1974)
			*					Zubovic et al (1960)
			***					Horton et al (1950)
			*					Breger et al (1955)

Table 6

Barium

Organic			Not Significant				Inorganic	
p<.0001	.001	.01	.05	1.0	.05	.01	.001 <.0001	
							*	Miller (1977)
				**			*	Kuhn et al (1980)

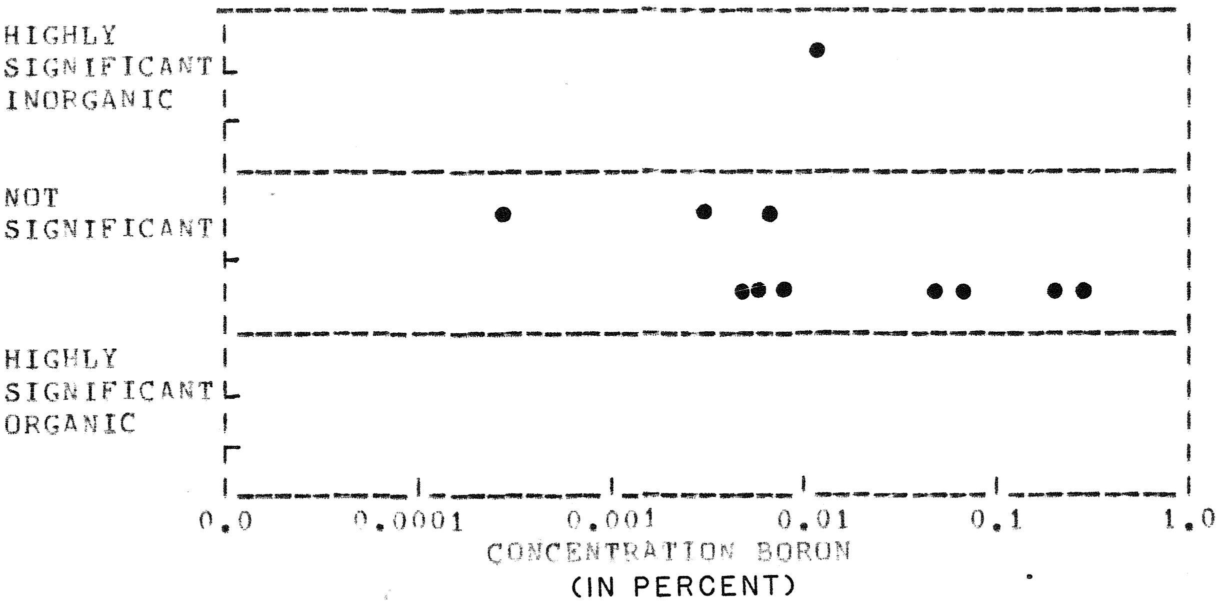

FIGURE 3

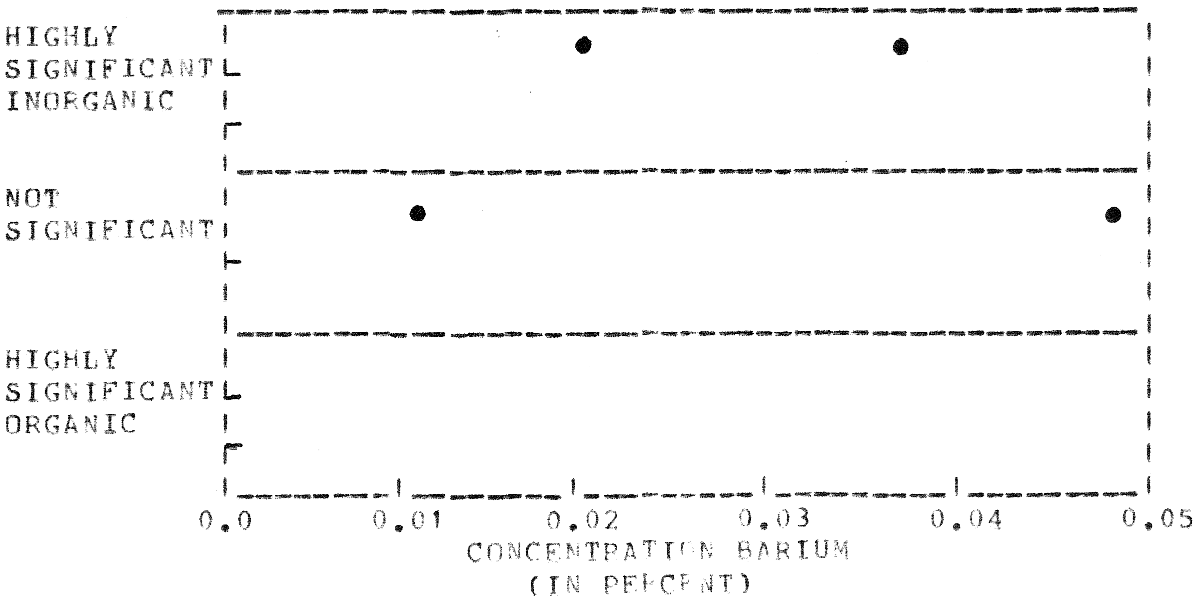

FIGURE 4

Table 7

Magnesium

Organic Not Significant Inorganic

p<.0001–.001	.001–.01	.01–.05	.05–1.0	1.0–.05	.05–.01	.01–.001	.001–<.0001	
				***				Kuhn et al (1980)
				***			*	Ruch et al (1974)
*								Miller (1977)
			*					Breger et al (1955)

Table 8

Strontium

Organic Not Significant Inorganic

p<.0001–.001	.001–.01	.01–.05	.05–1.0	1.0–.05	.05–.01	.01–.001	.001–<.0001	
				**				Kuhn et al (1980)
*								Miller (1977)

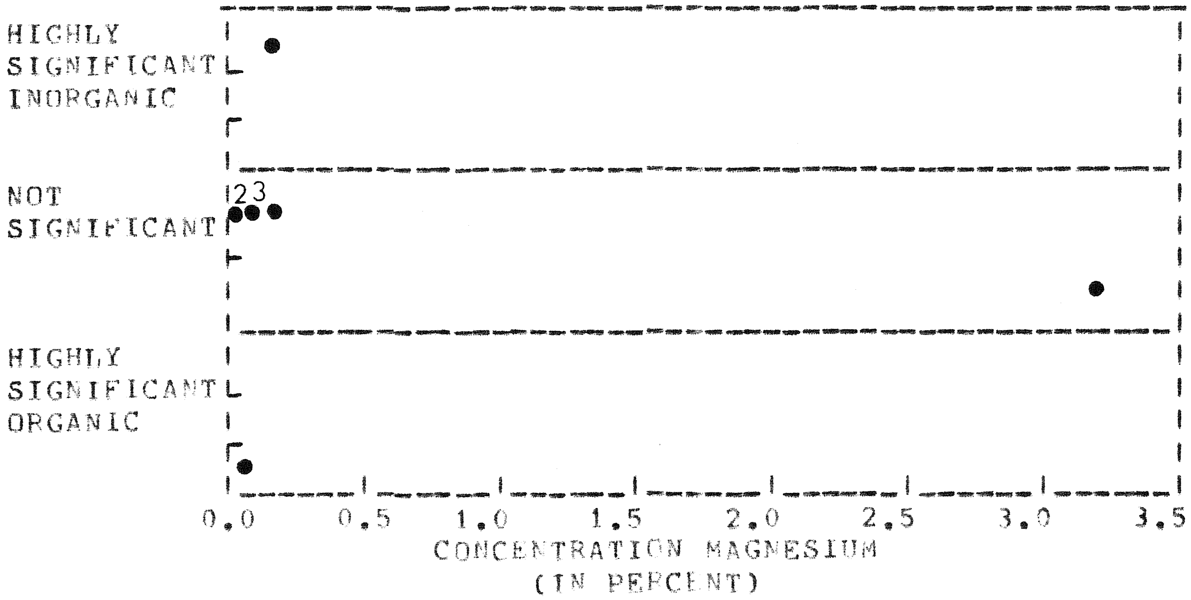

FIGURE 5

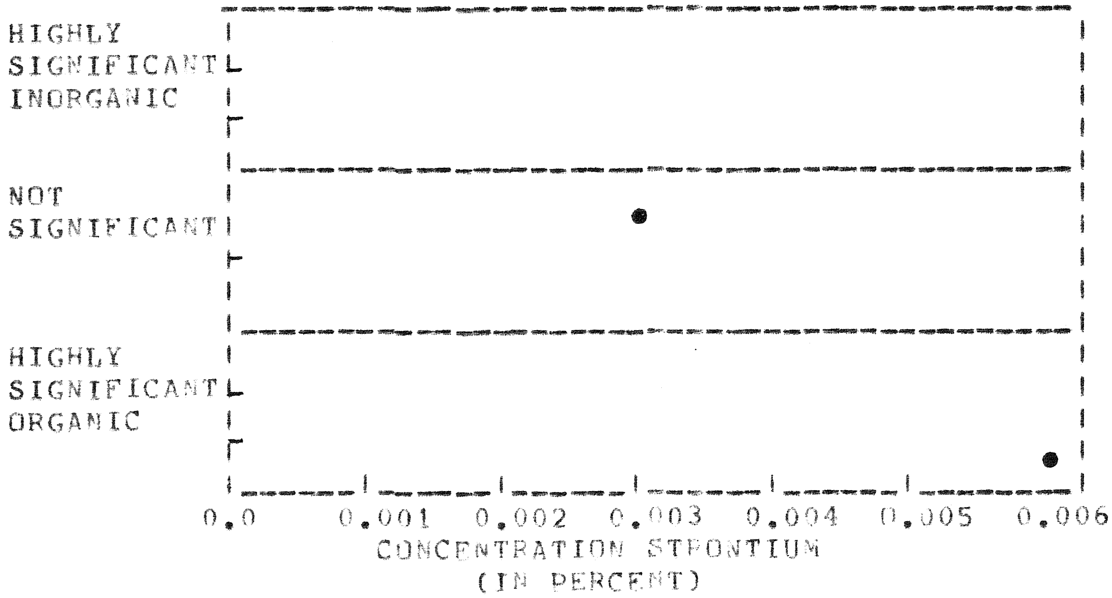

FIGURE 6

Although Nicholls (1968) agrees that strontium is variable in association in coal he mentions a relationship between strontium and carbonate content and describes some strontium to be adsorbed on clay minerals during the early stages of coal formation. But he concludes that the high strontium contents in coals is related to the introduction of post-depositional mineral matter. Strontium is also known to substitute for calcium in calcite (Mason and Berry, 1968). Strontium, summarized in Table 8 shows strontium to be inconsistent and attributable to random selection as predicted in Table 2.

Antimony in Table 2 is considered to be largely organically associated with the exception of the opinion of Ruch et al (1974). They found it to be variable in association. In Table 12 only the data of Horton and Aubrey (1950) show significant differences and they are organic in association. Antimony in figure 10 is organic in the higher concentration ranges.

Germanium has been extensively studied in the literature. Relative to the Earth's crust coal is known to contain high concentrations of germanium. Ratinskii (1943, 1946) and Otte (1953) found germanium to concentrate in the vitrains which have undergone the most gelification. It is these humic acid gels which entrap and concentrate the germanium brought in by aqueous solutions during the decomposition of the original plant material during the peat stage. Fischer (1960) suggested the following conclusions which are related to the association of germanium in coal:

1)Coals high in vitrain content contain more germanium than those with low vitrain content.
2)Low-ash coals are richer in germanium than high-ash coals.
3)Coals of older age usually have lower germanium content than coals which are more recent.
4)Germanium is usually concentrated in the top and bottom portions of a coal seam.

In Table 2 germanium is considered organic in association by the authors listed with the exception of Nicholls who considers it to be variable. Table 13 shows Ruch's et al (1974) germanium values show a highly significant differentiation and the major amount is organic in association. The other numbers are not significant but concentrations of germanium in Horton et al (1950) and Breger et al (1955) indicate that concentrations were higher in the inorganic fraction than the organic fraction. Perhaps the scatter of germanium is related to variations such as suggested by Fischer (1960). Germanium shows an organic association at lower concentration ranges in figure 11.

Table 9

Manganese

Organic Not Significant Inorganic

p<.0001	.001	.01	.05	1.0	.05	.01	.001	<.0001	
				**	*				Kuhn et al (1980)
				**				**	Ruch et al (1974)
				***					Horton et al (1950)
								*	Miller (1977)
			*						Breger et al (1955)

Table 10

Sodium

Organic Not Significant Inorganic

p<.0001	.001	.01	.05	1.0	.05	.01	.001	<.0001	
				**	*				Kuhn et al (1980)
				**	*				Ruch et al (1974)
*									Miller (1977)
			*						Breger et al (1955)

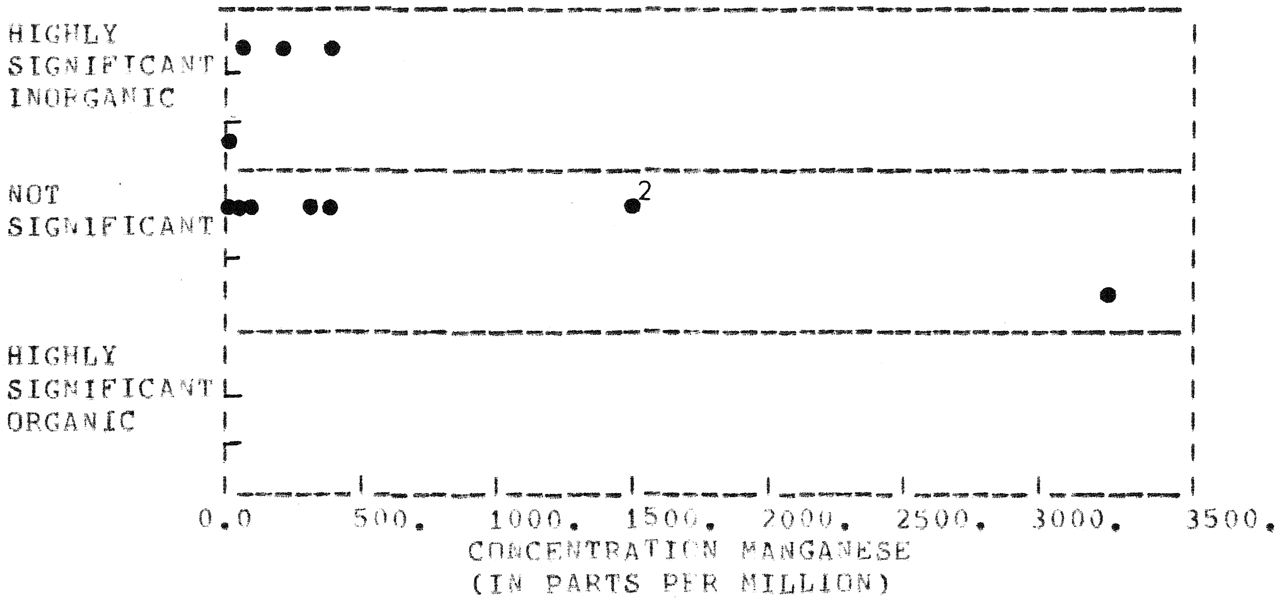

FIGURE 7

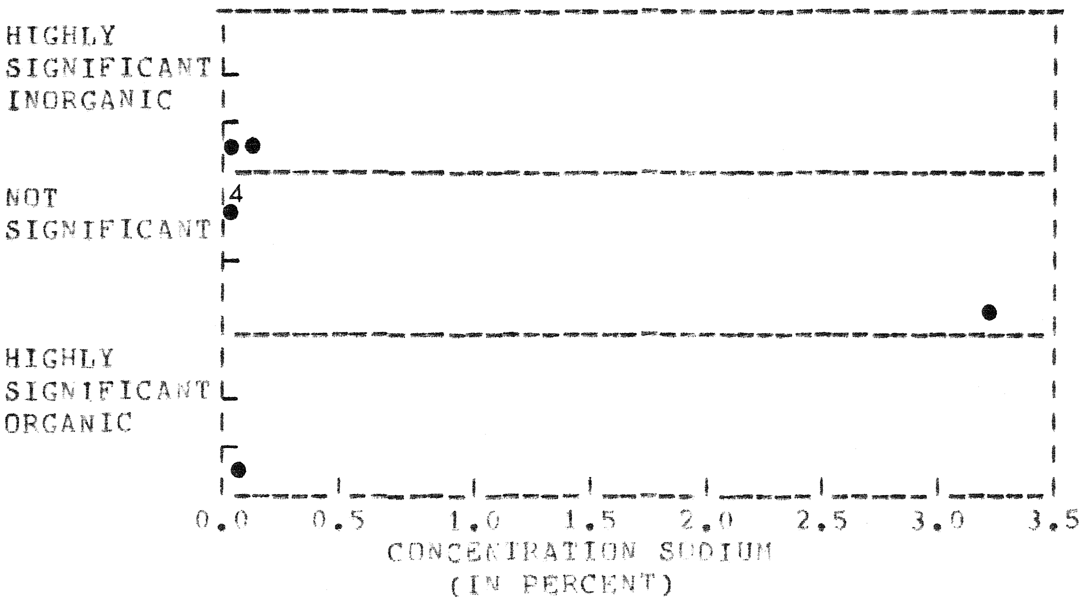

FIGURE 8

Table 11

Potassium

Organic			Not Significant		Inorganic			
p<.0001	.001	.01	.05	1.0	.05	.01	.001 <.0001	
				*				Kuhn et al (1980)
					*			Ruch et al (1974)
			*					Miller (1977)

Table 12

Antimony

Organic			Not Significant		Inorganic			
p<.0001	.001	.01	.05	1.0	.05	.01	.001 <.0001	
				***				Kuhn et al (1980)
				****				Ruch et al (1974)
*			*					Horton et Al (1950)

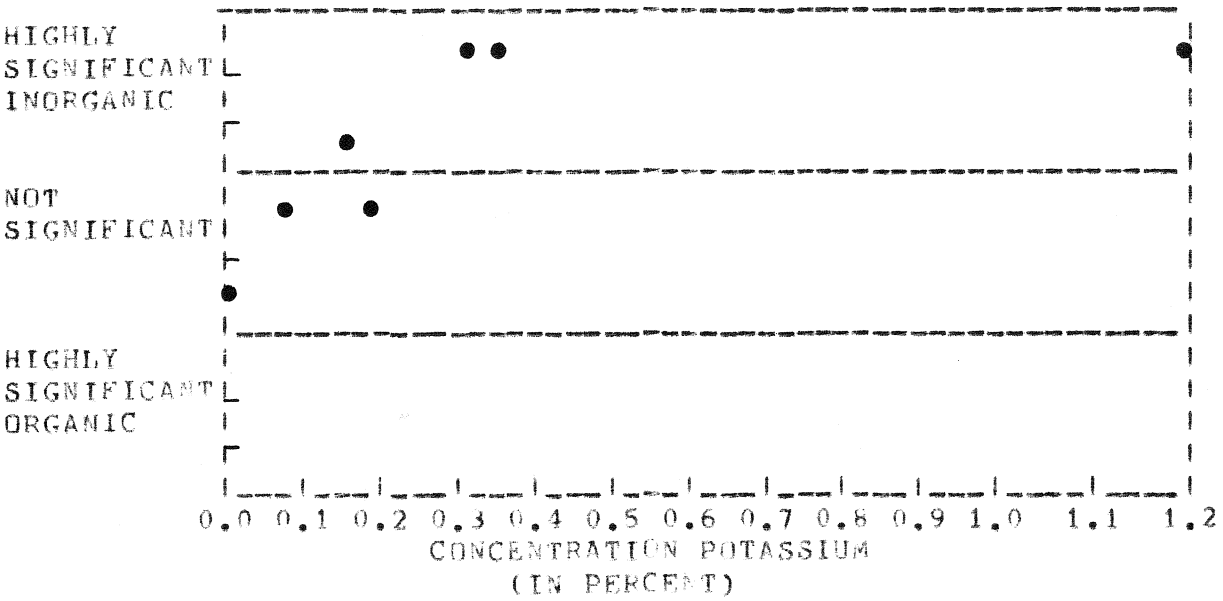

FIGURE 9

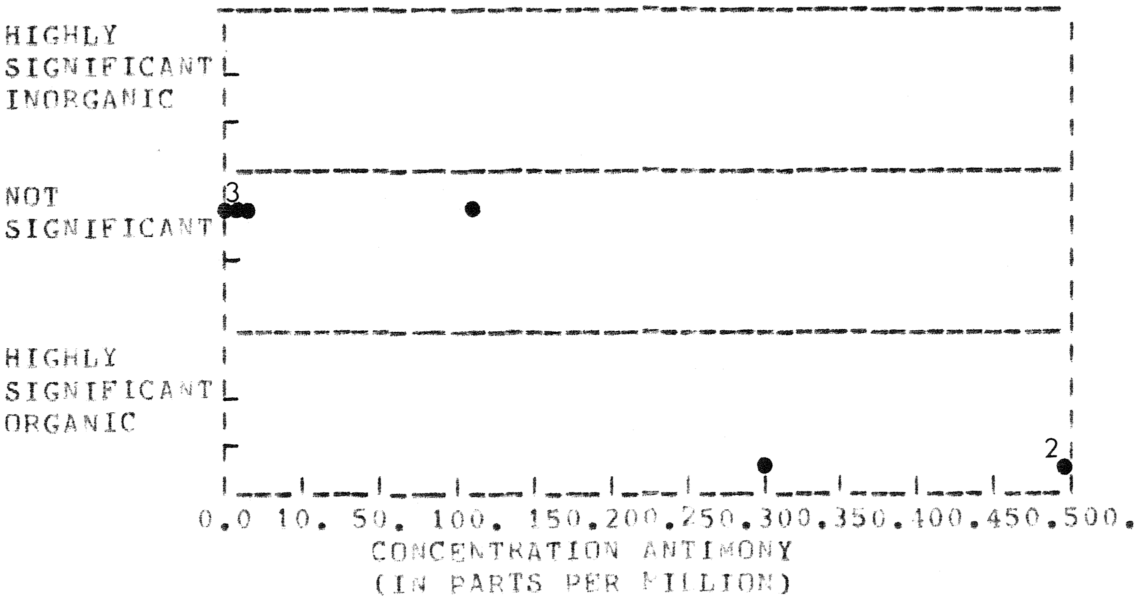

FIGURE 10

Beryllium is another element considered to be organically associated. In Table 2 this is evident except for Bogdanov who considers it to be inorganic. Otte (1953) found beryllium to be concentrated chiefly in vitrains and clarains. Stadnichenko, Zubovic, and Sheffey (1961) found the beryllium content from the ash of vitrains to be higher than its content in the ash of the whole coal. They also determined that the amount of beryllium in coal is unrelated to the rank and age of the coal. Beryllium content is related to the source of the various rocks that may have contributed to the coal deposit, and position in the basin. Because of its chemical properties, beryllium can be transported to the site of deposition and become incorporated into the coal syngenetically rather than post-depositionally. Beryllium has also been correlated with ash content. Jedwals (1960) found that coals with high beryllium content generally have low ash. Beryllium is known to form beryllium-organic complexes and combines with oxygen as the donor element (Martell and Calvin, 1952). Stadichenko et al (1961) hypothesizes the presence of organic beryllium to be the result of plant accumulation or due to fixation by adsorption onto colloidal organic particles in the swamp or by beryllium-organic complexes with the decomposed plant tissues.

The probability of beryllium in Table 14 concentrating significantly with either the organic or inorganic fractions is low. This indicates that the results are due to random selection and that the tests for beryllium are the results of unknown factors. The probability vs concentration plot of beryllium is shown in figure 12.

Nickel as it has been summarized in Table 2 is inconsistent in its association in coal. This inconsistency is reflected in Table 15. Although the results of 3 authors in Table 15 indicate that nickel is inorganic and 2 authors in Table 15 indicate that there is a higher concentration of nickel in the organic portion of the coal, only the work of Ruch et al (1974) has highly significant differences in magnitude indicating that nickel is inorganic in association. Possible reasons for the conflicting evaluations may be the association of nickel with mineral matter as well as a necessary nutrient for plant life. Nickel has been described to be associated with the smectites and may substitute for aluminum in the octahedral sheet (Grim, 1968). Nickel is also known to substitute for iron in pyrite (Maclean and Shimazake, 1976; Mitchell, 1968; and Raisdell and Plant, 1980). Nickel is also found in other sulfide minerals such as millerite and linnaeite. Miller (1931) listed nickel among those elements necessary for plant life. Thus, nickel is contributed by both inorganic and organic sources and may indicate that nickel cannot be attributed to any one fraction of the coal. Figure 13 shows that nickel is inorganically associated at approximately the 0.05 percent concentration range.

Table 13

Germanium

Organic Not Significant Inorganic

p<.0001	.001	.01	.05 1.0	.05	.01	.001	<.0001	
*			***					Ruch et al (1974)
			*					Zubovic et al (1960)
			**	*				Horton et al (1950)
				*				Breger et al (1955)

Table 14

Beryllium

Organic Not Significant Inorganic

p<.0001	.001	.01	.05 1.0	.05	.01	.001	<.0001	
				**				Kuhn et al (1980)
				****				Ruch et al (1974)
			*					Zubovic et al (1960)
			***					Horton et al (1950)
			*					Miller (1977)
			*					Breger et al (1955)

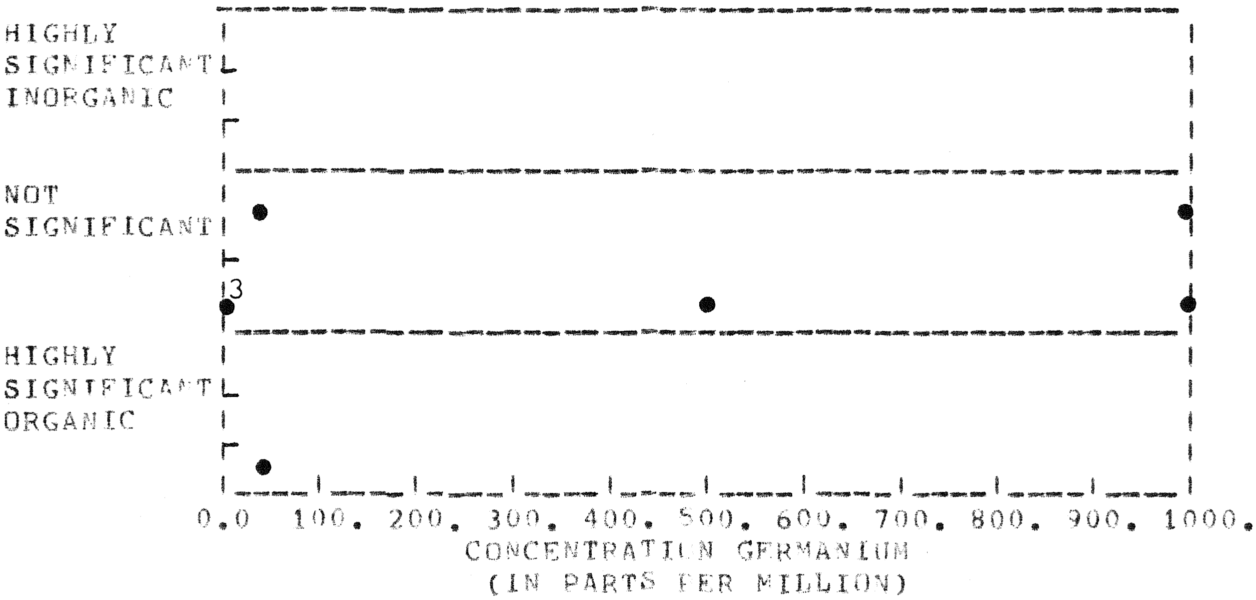

FIGURE 11

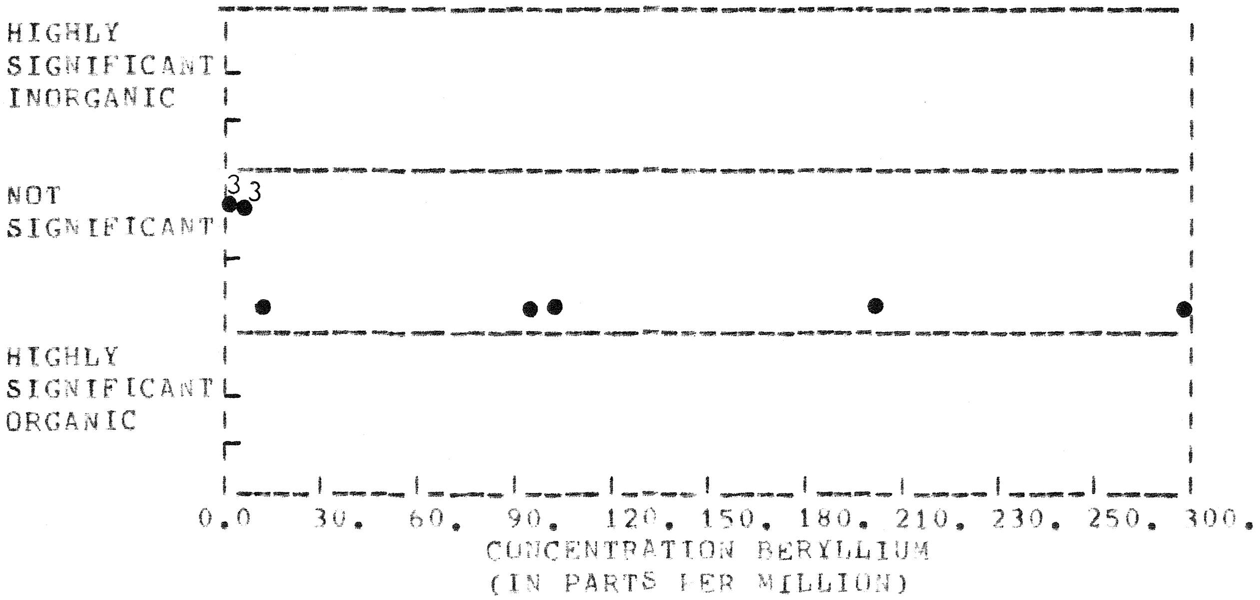

FIGURE 12

Table 15

Nickel

Organic Not Significant Inorganic

p<.0001	.001	.01	.05	1.0	.05	.01	.001	<.0001
				**				Kuhn et al (1980)
				*	*		**	Ruch et al (1974)
				*				Zubovic et al (1960)
			***					Horton et al (1950)
			*					Miller (1977)
			*					Breger et al (1955)

Table 16

Calcium

Organic Not Significant Inorganic

p<.0001	.001	.01	.05	1.0	.05	.01	.001	<.0001
				**			*	Kuhn et al (1980)
				**			**	Ruch et al (1974)
*								Miller (1977)
			*					Breger et al (1955)

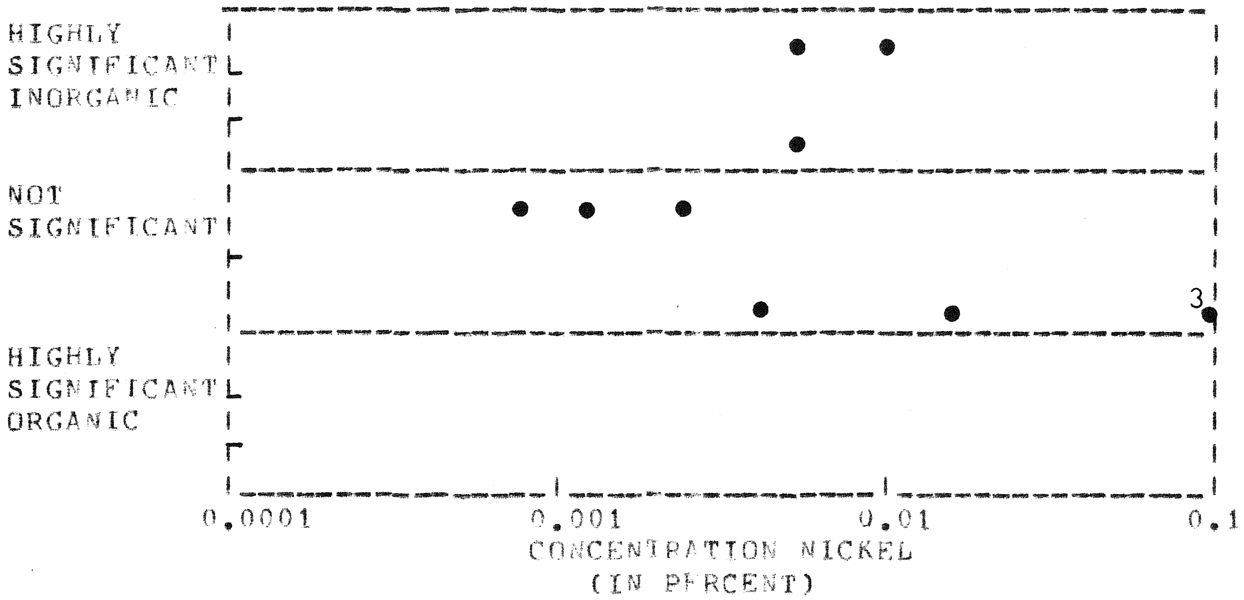

FIGURE 13

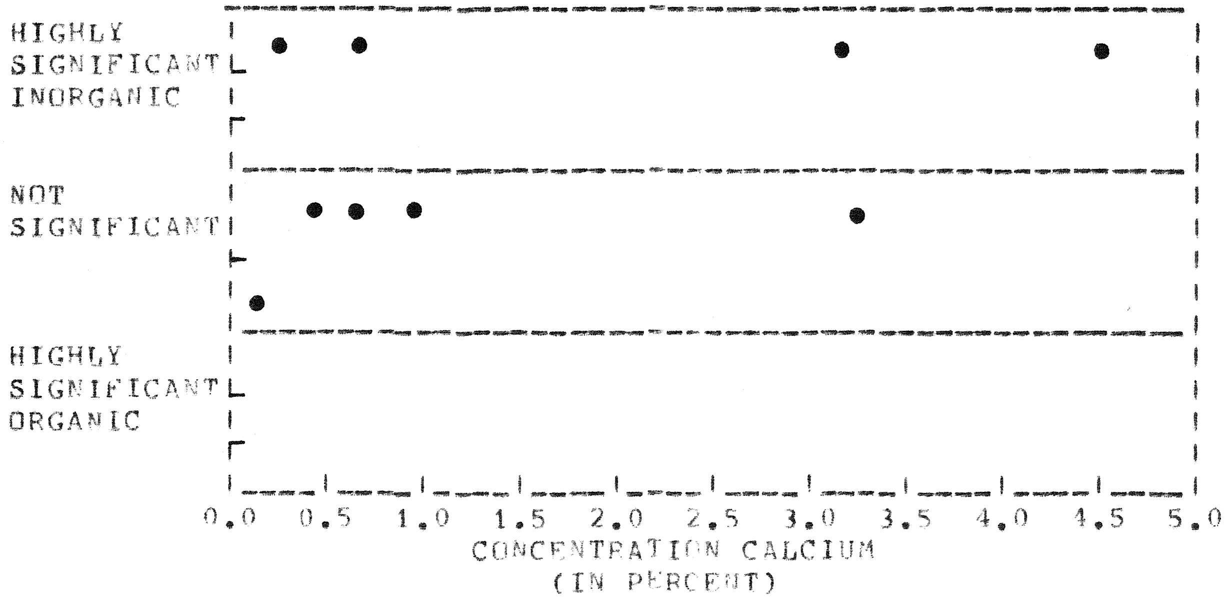

FIGURE 14

Calcium is another element similar to nickel in that it is both important as an organic as well as an inorganic substance. Miller (1931) and Kuhn et al (1980) attribute calcium to be necessary for the growth of all plants. Calcium is also present in carbonate minerals. The carbonates are very important mineral constituents in coal because they are the next most abundant after the clay minerals (Stach, 1975). In Table 2, only Miller (1977) concludes that calcium is organic in association. Other authors listed in Table 2 make no conclusions. In the case of Kuhn et al (1980) and Ruch et al (1974), calcium is highly significantly inorganic as shown in Table 16. Calcium, is highly significantly organic determined by analysis of Miller's (1977) work. Figure 14 supports calcium as an inorganicallyy associated element at various concentration ranges.

This split in the association of calcium reflects the known association of calcium with both the organic and inorganic portions of the coal. Carbonates can form authigenetically in the pre-burial stage of coal formation (Miller, 1977) and epigenetically as inferred by their location in cleavage, joint and fracture planes (Marshall,1955).

Vanadium in Table 2 is inconsistent in association. Miller (1977) accounts for the presence of a small portion of vanadium in the sink fraction as present in clay minerals. The majority of the vanadium he reports to be organically held by chelation or ion exchange. Table 17 shows consistent agreement between 3 of the authors. Their numbers are highly significant and suggest an inorganic association. From these results it may be possible to state that vanadium is commonly inorganically associated. it may well reflect the influence of marine waters. Figure 15 shows that vanadium is inorganic at low concentration ranges.

Most of the authors in Table 2 agree that gallium is variable in association. Only Inagaki (1968) has found this element to be inorganic. The random variability test in Table 18 reinforces this variability in the analysis of the data of Ruch et al (1974). In their probabilities, there is a highly significant inorganically associated gallium value as well as an insignificant organic value. The other tests show a similar insignificant differentiation. Goldschmidt (1954) determined that because of gallium's ionic radius and ionic charge it could enter the silicate lattice and substitute for aluminum in aluminosilicates. Gallium, studied by Dalton and Pringle (1962), is often similar to germanium as there is a tendency for it to concentrate near the roof and floor of coal seams. Dalton and Pringle (1962) use Headlee and Hunter's (1951) explanation that this localization is the result of percolating water and capillary action from above and below, respectively. Gallium is associated with the aluminosilicates which are intimately mixed with the coal and derived from mineral matter absorbed by the coal forming plants (Dalton and Pringle, 1962). Gallium, as shown in figure 16, is inorganic at low concentration values.

Table 17

Vanadium

Organic			Not Significant				Inorganic	
p<.0001	.001	.01	.05	1.0	.05	.01	.001 <.0001	
				**			*	Kuhn et al (1980)
				*		**	*	Ruch et al (1974)
							*	Szilagyi (1971)
			*					Zubovic et al (1960)
			***					Horton et al (1950)
			*					Miller (1977)

Table 18

Gallium

Organic			Not Significant				Inorganic	
p<.0001	.001	.01	.05	1.0	.05	.01	.001 <.0001	
				**				Kuhn et al (1980)
			*	*			**	Ruch et al (1974)
				*				Dalton et al (1962)
			*					Zubovic et al (1960)
			***					Horton et al (1950)

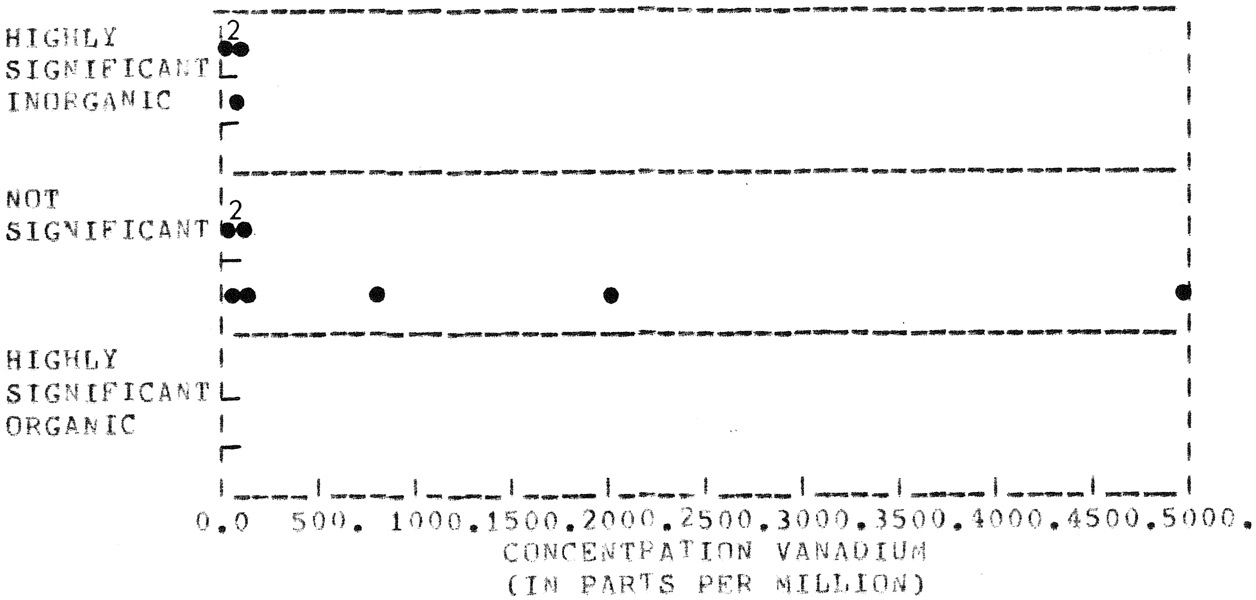

FIGURE 15

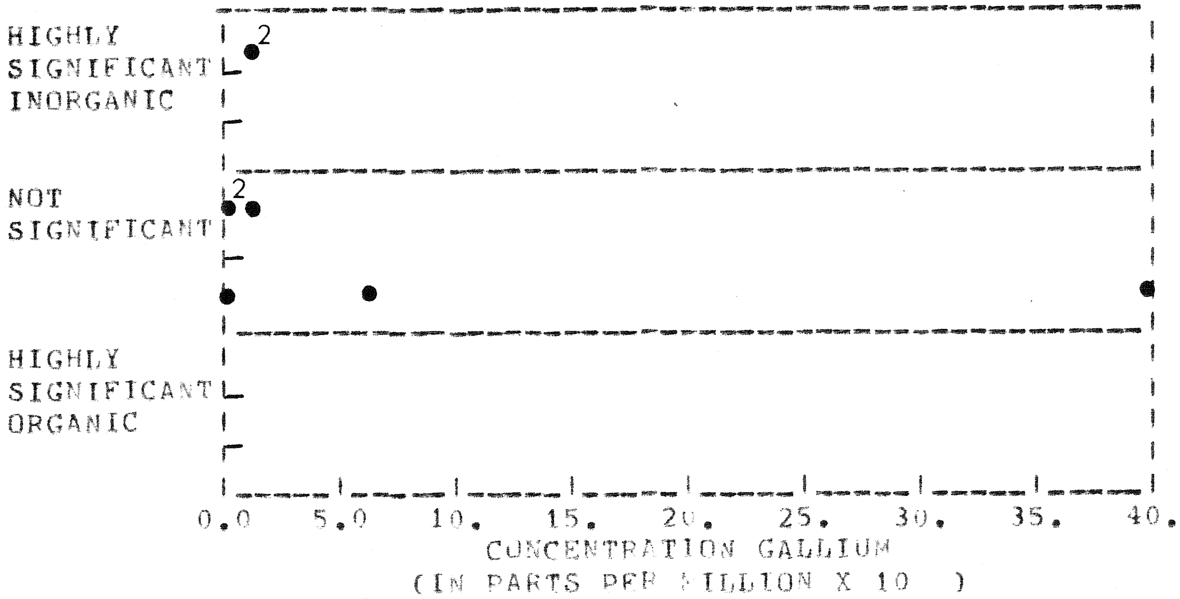

FIGURE 16

To test the sensitivity of this type of statistical analysis, silicon was analyzed for the various authors who have presented data relating silicon's association in coal. Silicon is the major contribution to the inorganic or mineral matter portion of the coal and is found in all of the silicate minerals associated with coal. A small amount of silicon is also associated with the organic portion of coal as inherent mineral matter. Since the greater quantity is associated with the mineral matter, sink float tests should show silicon to be inorganic in association. Table 19 shows highly significant and very significant inorganically associated probabilities for two of the authors tested. The other probabilities, although they are not significant, are also inorganic in their distribution. Silicon is inorganic throughout the entire concentration range (figure 17).

Titanium in Table 2 has probabilities suggesting inconsistent in its association. The results of Table 20 show highly significant probabilities for both organic and inorganic association in the coals tested. The data of Ruch et al (1974) shows a very significant probability that titanium is inorganically associated. The results of the other authors are not significant. Miller and Given (1978) as a result of their work believe titanium to be associated with the organic matter rather than the mineral phases based on their acid solubility tests. Organo-titanium complexes in coals have even been suggested (Zubovic et al, 1960; and Given et al, 1975). Titanium is also known to be associated in such minerals as rutile, anatase, brookite, ilmenite, and sphene. High concentrations of heavy minerals probably produce a concentration of titanium with the inorganic fraction whereas the acid-solubility testing of Miller and Given suggests normal titanium would be organic. Titanium has no characteristic distribution based on the probability versus concentration plot shown in figure 18.

Gluskoter et al (1977) suggest that selenium may be inherited from plants which have concentrated it in the original coal swamp. Selenium was one of the elements used by Mitchell (1968) to distinguish between marine pyrite, magmatic/hydrothermal, and fresh-water pyrites. He noted that among other elements selenium was higher in concentration in marine pyrite than fresh-water pyrites. Table 2 describes selenium as variable in association, while Table 21 shows the probability of selenium being inorganicis highly significant The results of these tests indicate that selenium may be inorganic in association rather than variable. Selenium as shown in figure 19 is inorganic at higher concentration values.

In Table 2 molybdenum is inconsistent in its distribution between the different coal fractions. In Table 22, although there is variability, analyses of several authors indicates molybdenum a highly significant level is inorganic in association. The data of Horton et al (1950) and Breger et al (1968) indicate an organic association but their data are not significantly different. Nicholls (1968) hypothesizes that molybdenum may be associated with sulfide minerals of coal seams and adds that some molybdenum which is found in the light fractions may be the result of post-burial sorption similar to germanium. Korolev (1955) investigated the

Table 19

Silicon

Organic Not Significant Inorganic

p<.0001	.001	.01	.05	1.0	.05	.01	.001 <.0001	
				*		*	*	Kuhn et al (1980)
					*	*	**	Ruch et al (1974)
				*				Breger et al (1955)

Table 20

Titanium

Organic Not Significant Inorganic

p<.0001	.001	.01	.05	1.0	.05	.01	.001 <.0001	
				***				Kuhn et al (1980)
						*	*	Ruch et al (1974)
			*					Zubovic et al (1960)
			**					Horton et al (1950)
*								Miller (1977)
			*					Breger et al (1955)

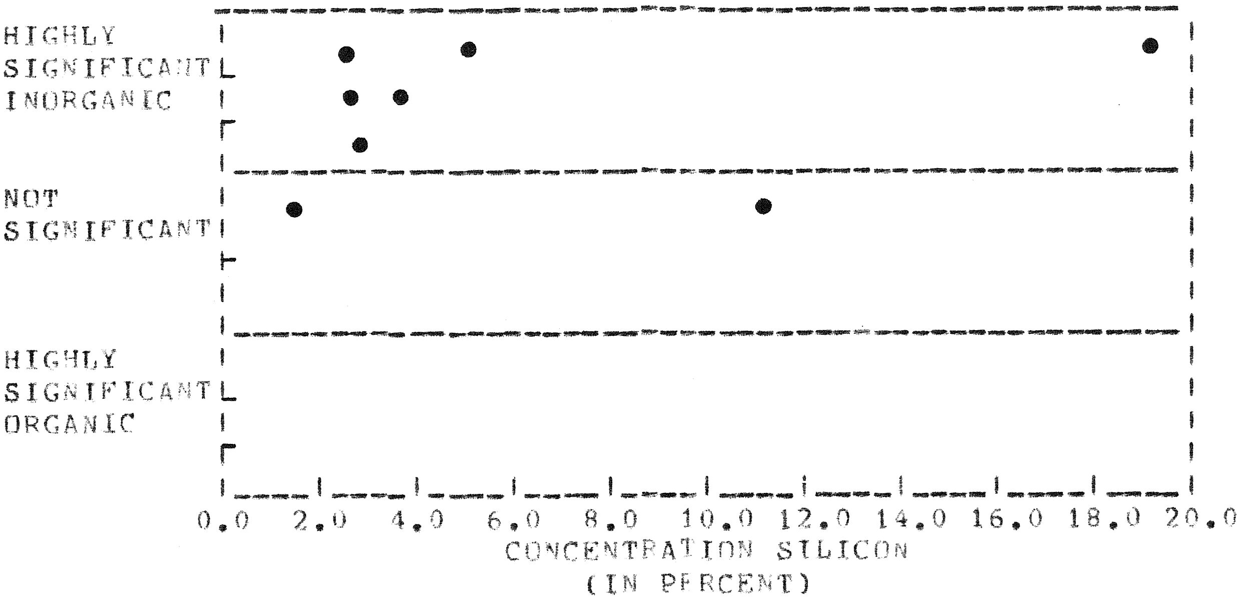

FIGURE 17

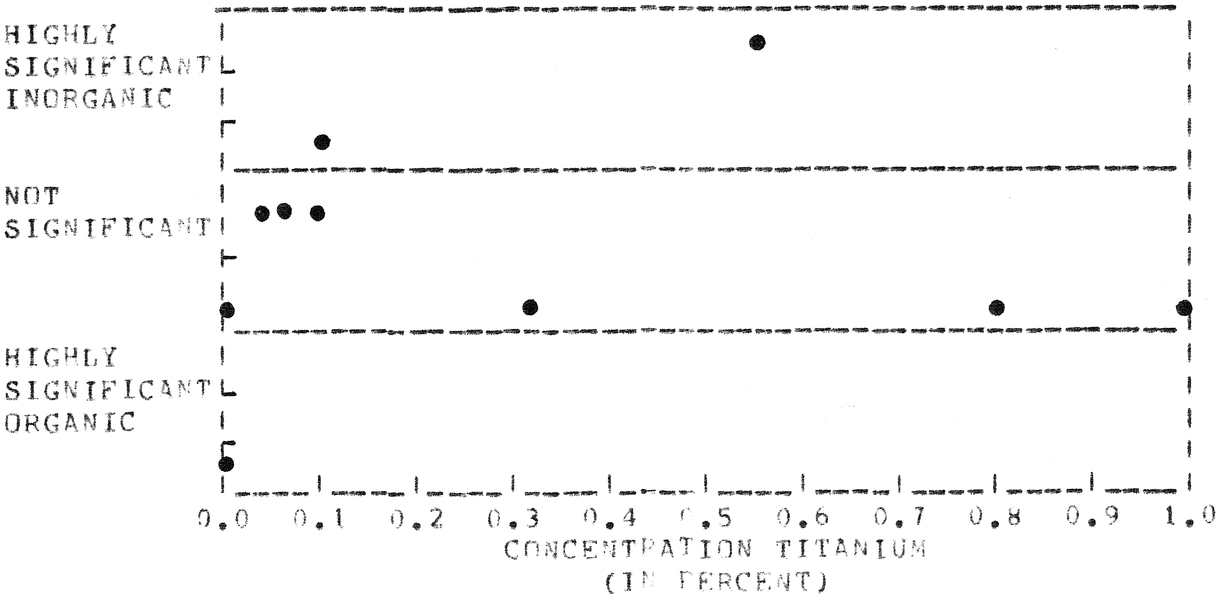

FIGURE 18

Table 21

Selenium

Organic Not Significant Inorganic

p<.0001 .001 .01 .05 1.0 .05 .01 .001 <.0001

				***				Kuhn et al (1980)
				*		*	**	Ruch et al (1974)

Table 22

Molybdenum

Organic Not Significant Inorganic

p<.0001 .001 .01 .05 1.0 .05 .01 .001 <.0001

				*				Kuhn et al (1980)
					*	*	**	Ruch et al (1974)
							**	Szilagyi (1971)
				*				Zubovic et al (1960)
			***					Horton et al (1950)
			*					Breger et al (1955)

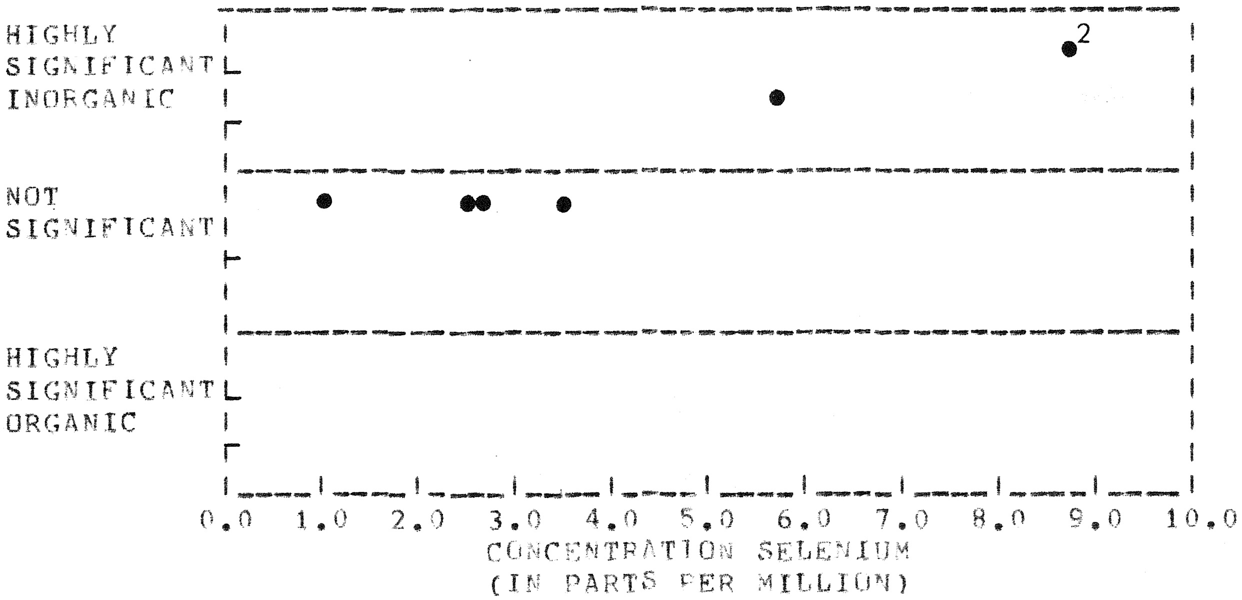

FIGURE 19

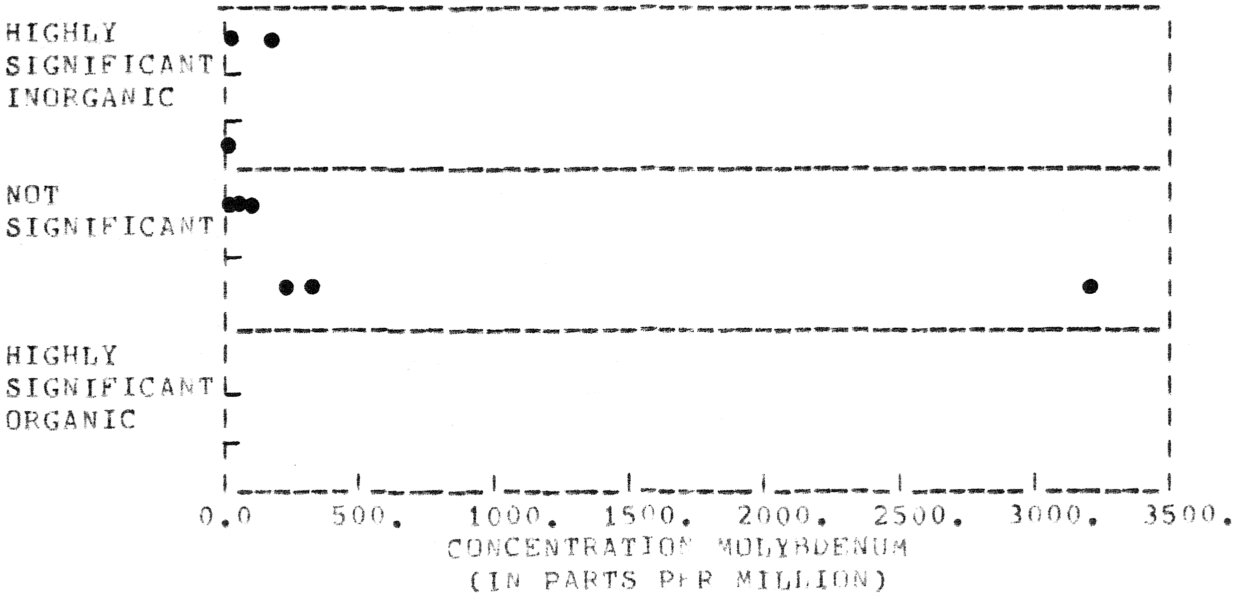

FIGURE 20

irregular accumulation of molybdenum in coals and concluded that in a coal where molybdenum is not directly bonded by organic matter its accumulation depends to a great extent on the intensity of the reduction process. The results in Table 23 are consistent. Even though molybdenum is often considered variable in association, the results in Table 22 indicate that the molybdenum in the coals studied by these authors is fairly consistently associated with the inorganic fraction.

Zirconium in Table 2 is summarized as inorganic in its association in coal. Table 23 shows the random variability test of zirconium data. The data show no significant and there appear to be no criteria with which to determine the association of zirconium. Zubovic (1966) explains that because of the ionic potential of zirconium it is largely associated with the mineral phases in coal as the heavy mineral zircon or isomorphically in clays (Mackowsky, 1968). Miller (1977) has found zirconium to exhibit a strong organic affinity in lignite. Zirconium forms stable complexes with carboxyl acid groups (Cotton and Wilkenson, 1966). Although zirconium is described as being inorganic in association in Table 2, the data in Table 23 do not support this interpretation. Figure 21 shows the probability versus concentration plot of Zircinium. No trend is apparent from this figure.

In Table 2 all authors agree that copper is variable in association while zinc is inconsistent in its association. Table 24, showing the probabilities of copper's association with either fraction, also differ. The probabilities of Ruch et al (1974) indicate that the copper data tested show highly significant

Appendix 2:
(Continued)

KUHN,FIENE,CAHILL,GLUSKOTER AND SHIMP
ILLINOIS, EASTERN AND WESTERN COALS
[IN PERCENT]

ELEMENT	SEAM	LIGHT FRACTION (X)	HEAVY FRACTION (Y)	Z-VALUE (Z)	TWO-SIDED PROBABILITY (P)
V	EASTERN	0.00093	0.0038	-0.0056	.9920
V	HERRIN(#6)	0.00065	0.0030	-0.688	.4966
V	WESTERN	0.00023	0.00147	-3.426	.0006***
W	EASTERN	0.000026	0.000031	-0.0406	.9680
W	HERRIN(#6)	-	-	-	-
W	WESTERN	-	-	-	-
Yb	EASTERN	0.000019	0.000039	-0.5456	.5892
Yb	HERRIN(#6)	0.000013	0.000045	-0.85	.3954
Yb	WESTERN	0.000011	0.000028	-0.47	.6384
Zn	EASTERN	-	-	-	-
Zn	HERRIN(#6)	-	-	-	-
Zn	WESTERN	-	-	-	-

Appendix 3:

RUCH, GLUSKOTER AND SHIMP(1974)
ILLINOIS COALS
[IN PARTS PER MILLION]
[UNLESS INDICATED]

ELEMENT	SEAM	LIGHT FRACTION (X)	HEAVY FRACTION (Y)	Z-VALUE (Z)	TWO-SIDED PROBABILITY (P)
Al	COLCHESTER(#2)	0.26%	3.05%	-5.332	<.0001***
Al	DAVIS MEMBER	0.43%	1.39%	-1.834	.0672
Al	DEKOVEN	0.53%	1.50%	-1.854	.0644
Al	HERRIN(#6)	0.41%	9.50%	-17.372	<.0001***
As	COLCHESTER(#2)	14.0	630.0	-1.603	.1096
As	DAVIS MEMBER	0.7	58.00	-2.25	.0244*
As	DEKOVEN	2.9	181.0	-6.649	<.0001***
As	HERRIN(#6)	0.9	58.0	-2.131	.0332*
B	COLCHESTER(#2)	70.0	42.0	0.541	.5824
B	DAVIS MEMBER	29.0	80.00	0.342	.7338
B	DEKOVEN	35.0	-	-	-
B	HERRIN(#6)	90.0	80.0	0.136	.8886
Be	COLCHESTER(#2)	2.6	7.0	-0.014	.9920
Be	DAVIS MEMBER	2.8	3.2	0.852	.3954
Be	DEKOVEN	7.0	7.1	-0.085	.3954
Be	HERRIN(#6)	2.3	3.2	-0.766	.4412
Ca	COLCHESTER(#2)	0.07%	4.53%	-6.436	<.0001***
Ca	DAVIS MEMBER	0.21%	0.41%	-0.288	.7794
Ca	DEKOVEN	0.18%	0.03%	0.216	.8258
Ca	HERRIN(#6)	0.06%	3.20%	-4.531	<.0001***
Cd	COLCHESTER(#2)	0.1	338.0	-38.13	<.0001***
Cd	DAVIS MEMBER	0.1	27.0	-16.98	<.0001***
Cd	DEKOVEN	0.1	2.4	-0.195	.8494
Cd	HERRIN(#6)	0.2	27.0	-2.278	.0232*
Co	COLCHESTER(#2)	5.0	18.0	-0.262	.7948
Co	DAVIS MEMBER	2.0	19.00	-0.736	.4654
Co	DEKOVEN	12.0	19.0	-0.859	.3844
Co	HERRIN(#6)	2.0	19.0	-2.087	.0358*
Cr	COLCHESTER(#2)	4.0	40.0	-4.019	<.0001***
Cr	DAVIS MEMBER	7.0	71.00	-1.32	.1868
Cr	DEKOVEN	15.0	44.0	-2.741	.0062**
Cr	HERRIN(#6)	8.0	71.0	-5.955	<.0001***

Appendix 3:
(Continued)

RUCH,GLUSKOTER AND SHIMP(1974)
ILLINOIS COALS
[IN PARTS PER MILLION]
[UNLESS INDICATED]

ELEMENT	SEAM	LIGHT FRACTION (X)	HEAVY FRACTION (Y)	Z-VALUE (Z)	TWO-SIDED PROBABILITY (P)
Cu	COLCHESTER(#2)	17.00	140.0	-13.22	<.0001***
Cu	DAVIS MEMBER	4.0	65.0	-1.46	.1444
Cu	DEKOVEN	7.0	17.0	-1.042	.2984
Cu	HERRIN(#6)	5.0	65.0	-6.257	<.0001***
Fe	COLCHESTER(#2)	1.19%	21.21%	-19.938	<.0001***
Fe	DAVIS MEMBER	0.51%	26.10%	-25.485	<.0001***
Fe	DEKOVEN	0.85%	6.64%	-5.766	<.0001***
Fe	HERRIN(#6)	0.54%	9.88%	-9.302	<.0001***
Ga	COLCHESTER(#2)	2.4	13.0	-3.897	<.0001***
Ga	DAVIS MEMBER	1.1	12.0	-0.411	.6818
Ga	HERRIN(#6)	2.1	12.0	-6.796	<.0001***
Ga	DEKOVEN	3.7	3.1	0.4119	.6818
Ge	COLCHESTER(#2)	31.0	10.0	2.483	<.0001***
Ge	DAVIS MEMBER	9.0	1.00	0.499	.6170
Ge	DEKOVEN	10.0	6.0	0.3995	.6892
Ge	HERRIN(#6)	15.0	1.0	1.398	.1646
K	COLCHESTER(#2)	0.05%	0.36%	-5.480	<.0001***
K	DAVIS MEMBER	0.06%	0.07%	-0.177	.4325
K	DEKOVEN	0.08%	0.31%	-4.065	<.0001***
K	HERRIN(#6)	0.06%	1.20%	-20.152	<.0001***
Mg	COLCHESTER(#2)	0.001%	0.010%	-0.318	.7566
Mg	DAVIS MEMBER	0.020%	0.170%	-5.303	<.0001***
Mg	DEKOVEN	0.003%	0.010%	-0.247	.8026
Mg	HERRIN(#6)	0.003%	0.030%	-0.954	.3422
Mn	COLCHESTER(#2)	5.0	209.0	-4.839	<.0001***
Mn	DAVIS MEMBER	8.0	365.0	-1.259	.2112
Mn	DEKOVEN	8.0	26.00	-0.310	.7566
Mn	HERRIN(#6)	7.0	365.0	-6.177	<.0001***
Mo	COLCHESTER(#2)	2.0	111.0	-0.798	.4296
Mo	DAVIS MEMBER	2.0	28.0	-7.345	<.0001***
Mo	DEKOVEN	3.0	135.0	-16.432	<.0001***
Mo	HERRIN(#6)	5.0	28.0	-2.863	.0042**

Appendix 3:
(Continued)

RUCH, GLUSKOTER AND SHIMP (1974)
ILLINOIS COALS
[IN PARTS PER MILLION]
[UNLESS INDICATED]

ELEMENT	SEAM	LIGHT FRACTION (X)	HEAVY FRACTION (Y)	Z-VALUE (Z)	TWO-SIDED PROBABILITY (P)
Na	COLCHESTER(#2)	0.008%	0.020%	-0.212	.8336
Na	DAVIS MEMBER	0.010%	0.020%	-0.176	.8650
Na	DEKOVEN	0.010%	0.010%	-	-
Na	HERRIN(#6)	0.020%	0.140%	-2.121	.0348*
Ni	COLCHESTER(#2)	16.0	116.0	-8.774	<.0001***
Ni	DAVIS MEMBER	9.0	77.0	-2.420	.0156*
Ni	DEKOVEN	18.0	38.0	-1.308	.1902
Ni	HERRIN(#6)	9.0	77.0	-4.448	<.0001***
P	COLCHESTER(#2)	21.0	14.0	22.913	<.0001***
P	DAVIS MEMBER	13.0	-	-	-
P	DEKOVEN	81.0	167.0	-	-
P	HERRIN(#6)	-	-	-	-
Pb	COLCHESTER(#2)	81.0	753.0	-14.57	<.0001***
Pb	DAVIS MEMBER	12.0	530.0	-14.99	<.0001***
Pb	DEKOVEN	15.0	880.0	-13.314	<.0001***
Pb	HERRIN(#6)	13.0	530.0	-7.957	<.0001***
Sb	COLCHESTER(#2)	3.9	110.0	-0.00	.1000
Sb	DAVIS MEMBER	0.3	4.2	-0.3486	.7338
Sb	DEKOVEN	0.6	0.8	-0.0996	.9204
Sb	HERRIN(#6)	1.2	4.2	-1.494	.1336
Se	COLCHESTER(#2)	0.8	3.5	-0.753	.4532
Se	DAVIS MEMBER	1.6	8.8	-3.649	<.0001***
Se	DEKOVEN	2.1	5.8	-2.813	.0050**
Se	HERRIN(#6)	1.1	8.8	-5.854	<.0001***
Si	COLCHESTER(#2)	0.49%	5.31%	-5.497	<.0001***
Si	DAVIS MEMBER	0.77%	3.62%	-3.250	.0012**
Si	DEKOVEN	0.78%	2.63%	-2.109	.0348*
Si	HERRIN(#6)	0.59%	19.35%	-21.395	<.0001***
Ti	COLCHESTER(#2)	0.03%	0.10%	-2.475	.0124*
Ti	DAVIS MEMBER	0.04%	0.04%	-	-
Ti	DEKOVEN	0.04%	0.04%	-	-
Ti	HERRIN(#6)	0.03%	0.56%	-18.738	<.0001***

Appendix 3:
(Continued)

RUCH,GLUSKOTER AND SHIMP(1974)
ILLINOIS COALS
[IN PARTS PER MILLION]
[UNLESS INDICATED]

ELEMENT	SEAM	LIGHT FRACTION (X)	HEAVY FRACTION (Y)	Z-VALUE (Z)	TWO-SIDED PROBABILITY (P)
V	COLCHESTER(#2)	8.0	46.0	-3.168	.0016**
V	DAVIS MEMBER	13.0	72.0	-0.7904	.4296
V	DEKOVEN	3.0	58.0	-3.344	.0008***
V	HERRIN(#6)	16.0	72.0	-3.404	.0032**
Zn	COLCHESTER(#2)	13.0	32140.0	-42.84	<.0001***
Zn	DAVIS MEMBER	31.0	3128.0	-2.352	.0188*
Zn	DEKOVEN	54.0	429.0	-0.353	.7264
Zn	HERRIN(#6)	7.0	3128.0	-2.943	.0032**
Zr	COLCHESTER(#2)	1.0	14.0	-0.219	.8336
Zr	DAVIS MEMBER	1.0	32.0	-0.207	.8336
Zr	DEKOVEN	2.0	19.0	-0.207	.8414
Zr	HERRIN(#6)	1.0	32.0	-0.3779	.7040

Appendix 4:

HORTON AND AUBREY(1950)
BRITISH COALS
(IN PERCENT)

ELEMENT	SEAM	LIGHT FRACTION (X)	HEAVY FRACTION (Y)	Z-VALUE (Z)	TWO-SIDED PROBABILITY (P)
B	DALTON MAIN	0.07	0.02	0.925	.3524
B	MARKHAM MAIN	0.5	0.3	0.3228	.6456
B	THURCROFT	0.08	0.02	0.986	.3222
Be	DALTON MAIN	0.01	0.006	0.751	.4468
Be	MARKHAM MAIN	0.02	0.015	0.2699	.7872
Be	THURCROFT	0.03	0.01	0.1977	.3954
Co	DALTON MAIN	0.05	0.03	0.462	.6456
Co	MARKHAM MAIN	0.03	0.02	0.604	.5486
Co	THURCROFT	0.03	0.05	0.462	.6456
Cr	DALTON MAIN	0.04	0.02	0.604	.5486
Cr	MARKHAM MAIN	0.04	0.02	0.604	.5486
Cr	THURCROFT	0.4	0.2	0.603	.5486
Cu	DALTON MAIN	0.1	0.07	0.653	.5156
Cu	MARKHAM MAIN	0.2	0.15	0.2699	.7872
Cu	THURCROFT	0.1	0.2	-0.269	.7872
Ga	DALTON MAIN	0.01	0.01	0.375	.7114
Ga	MARKHAM MAIN	0.04	0.015	0.7908	.4296
Ga	THURCROFT	0.04	0.03	0.271	.7872
Ge	DALTON MAIN	0.05	0.03	0.089	.9204
Ge	MARKHAM MAIN	0.1	0.08	0.211	.8236
Ge	THURCROFT	0.07	0.1	-0.331	.7642
Mn	DALTON MAIN	0.08	0.15	-0.556	.5754
Mn	MARKHAM MAIN	0.01	0.15	-0.374	.7114
Mn	THURCROFT	0.01	0.03	-0.866	.3844
Mo	DALTON MAIN	0.02	0.01	0.603	.5486
Mo	MARKHAM MAIN	0.03	0.01	0.854	.3954
Mo	THURCROFT	0.03	0.02	0.066	.9442
Ni	DALTON MAIN	0.1	0.07	0.331	.7414
Ni	MARKHAM MAIN	0.1	0.05	0.603	.5418
Ni	THURCROFT	0.3	0.4	0.21	.8336
P	DALTON MAIN	0.1	0.2	-0.269	.7872
P	MARKHAM MAIN	-	-	-	-
P	THURCROFT	0.4	1.5	-0.99	.3222

Appendix 4:
(Continued)

HORTON AND AUBREY(1950)
BRITISH COALS
[IN PERCENT]

ELEMENT	SEAM	LIGHT FRACTION (X)	HEAVY FRACTION (Y)	Z-VALUE (Z)	TWO-SIDED PROBABILITY (P)
Pb	DALTON MAIN	0.08	0.8	-	-
Pb	MARKHAM MAIN	0.07	0.04	0.5014	.6170
Pb	THURCROFT	0.05	0.1	-0.603	.5486
Sb	DALTON MAIN	0.05	0.008	-8.63	<.0001***
Sb	MARKHAM MAIN	0.03	0.3	-6.367	<.0001***
Sb	THURCROFT	0.05	0.03	0.464	.6456
Sn	DALTON MAIN	0.01	0.008	0.211	.8336
Sn	MARKHAM MAIN	0.02	0.008	0.752	.4532
Sn	THURCROFT	0.00	0.04	-1.06	.2892
Ti	DALTON MAIN	1.0	0.3	1.059	.3714
Ti	MARKHAM MAIN	1.0	1.0	-	-
Ti	THURCROFT	0.8	0.5	0.799	.4296
V	DALTON MAIN	0.08	0.04	0.6059	.5486
V	MARKHAM MAIN	0.2	0.1	0.603	.5418
V	THURCROFT	0.5	0.5	0.091	.4296
Zn	DALTON MAIN	0.05	0.1	-0.604	.5486
Zn	MARKHAM MAIN	0.05	0.0499	-0.017	-
Zn	THURCROFT	0.07	0.1	-0.331	.7414
Zr	DALTON MAIN	0.05	0.0099	1.06	.2714
Zr	MARKHAM MAIN	0.08	0.04	-0.017	.9840
Zr	THURCROFT	0.1	0.1	-	-

Appendix 5:

DALTON AND PRINGLE(1962) GALLIUM WARWICKSHIRE COALS [IN PARTS PER MILLION]

SEAM ELEMENT	LIGHT FRACTION (X)	HEAVY FRACTION (Y)	Z-VALUE (Z)	TWO-SIDED PROBABILITY (P)
WARWICKSHIRE COALFIELD				
UPPER SEAMS	6	27	-1.024	.3078
	6	41	-1.139	.2542
	5	30	-1.108	.2714
TWO YARDS	4	125	-1.305	.1936
BARE	3	42	-1.249	.2112
RYDER	4	53	-1.243	.2150
ELL	4	70	-1.269	.2076
NINE FEET	9	204	-1.288	.2006
HIGH MAIN	11	282	-1.295	.1970
SMITHY	3	35	-1.229	.2224
FLEET AND THIN	4	41	-1.211	
TRENCHER	5	85	-1.267	.2262
DEER RIDER	14	86	-1.115	.2670
DOUBLE	5	93	-1.274	.2040
TOP BENCH	9	96	-1.217	.2262
BENCH	4	70	-1.269	.2040
STANHOPE	7	109	-1.259	.2112
CANNOCK COALFIELD				
PARK	3	55	-1.273	.2040
DEEP	5	49	-1.205	.2302
YARD	11	168	-1.257	.2176
SHROPSHIRE COALFIELD				
TOP COAL	2	74	-1.311	.1902
NORTH STAFFSHIRE COALFIELD				
SPENCROFT	2	20	-1.207	.2302
YARD	5	50	-1.208	.2262

Appendix 5:
(Continued)

DALTON AND PRINGLE(1962)
GALLIUM WARWICKSHIRE COALS
[IN PARTS PER MILLION]

SEAM ELEMENT	LIGHT FRACTION (X)	HEAVY FRACTION (Y)	Z-VALUE (Z)	TWO-SIDED PROBABILITY (P)
SOUTH STAFFSHIRE COALFIELD				
THICK	8	136	-1.267	.2040
BROOCH	2	66	-1.307	.1902
FLYING REED	3	60	-1.279	.2006

Appendix 6:

SZILAGYI(1971)
HUNGARIAN COALS
[IN PPM]

SEAM ELEMENT	LIGHT FRACTION (X)	HEAVY FRACTION (Y)	Z-VALUE (Z)	TWO-SIDED PROBABILITY (P)
Mo MECSEK SEAM DEPTH IN SEAM				
0-10	13	166	-3.911	<.0001***
10-20	29	182	-4.584	<.0001***
20-30	34	131	-4.705	<.0001***
30-40	30	88	-3.668	<.0001***
40-50	50	112	-3.299	<.0012**
50-60	32	60	-1.788	.0734
60-70	37	57	-0.766	.5028
70-80	33	45	-0.304	.7642
80-90	15	19	-0.400	.6892
Mo BORSOD SEAM				
0-10	4	52	-1.409	.1586
10-20	5	53	-4.603	<.0001***
20-30	9	38	-5.687	<.0001***
30-40	11	32	-3.320	.0010**
40-50	12	26	-2.599	.0094
50-60	10	18	-1.372	.1706
60-70	6	9	-2.121	.0340*
70-80	5	7	-1.414	.1586
80-90	7	8	-0.141	.8886
V MECSEK SEAM				
0-10	26	327	-6.000	<.0001***
10-20	4	338	-6.518	<.0001***
20-30	83	324	-7.582	<.0001***
30-40	128	370	-7.151	<.0001***
40-50	183	411	-4.244	<.0001***
50-60	213	398	-3.726	<.0001***
60-70	192	297	-2.067	.0384*
70-80	283	382	-1.367	.1706
80-90	293	356	-0.693	.5902

Appendix 6:
(Continued)

SZILAGYI(1971)
HUNGARIAN COALS
[IN PPM]

SEAM ELEMENT	LIGHT FRACTION (X)	HEAVY FRACTION (Y)	Z-VALUE (Z)	TWO-SIDED PROBABILITY (P)
V BORSOD SEAM				
0-10	9	120	-1.787	.0734
10-20	33	219	-2.619	.0088*
20-30	49	199	-4.869	<.0001***
30-40	68	196	-5.059	<.0001***
40-50	112	250	-4.470	<.0001***
50-60	142	252	-2.824	.0048**
60-70	228	349	-2.260	.0238*
70-80	218	293	-1.543	.1236
80-90	206	242	-1.057	.2892
Cr MECSEK SEAM				
0-10	13	157	-4.953	<.0001***
10-20	24	153	-5.301	<.0001***
20-30	43	167	-4.605	<.0001***
30-40	54	157	-6.514	<.0001***
40-50	106	237	-4.434	<.0001***
50-60	117	219	-3.302	.0010**
60-70	110	170	-2.844	.0046*
70-80	108	146	-0.900	.3682
80-90	133	162	-0.783	.4354
Cr BORSOD SEAM				
0-10	4	60	-1.746	.0802
10-20	18	120	-2.968	.0030**
20-30	24	97	-4.702	<.0001***
30-40	42	120	-3.852	<.0001***
40-50	62	140	-3.556	<.0001***
50-60	97	172	-1.515	.1286
60-70	108	165	-2.536	.0114*
70-80	103	139	-1.935	.0536
80-90	85	100	-0.571	.5686

Appendix 7

DUCK AND HIMUS
AS IN COAL
[IN PPM]

DEPTH IN SEAM	LIGHT FRACTION (X)	HEAVY FRACTION (Y)	Z-VALUE (Z)	TWO-SIDED PROBABILITY (P)
A1	1.97	126.48	-6.6397	<.0001***
A2	0.403	34.46	-6.6656	<.0001***
AC1	0.805	46.20	-6.6197	<.0001***
AC2	0.599	43.17	-6.6510	<.0001***
SB1	1.68	14.01	-5.8937	<.0001***
SB2	0.616	12.49	-6.4035	<.0001***
SB3	1.82	257.5	-6.6970	<.0001***
B1	3.55	185.56	-6.1472	<.0001***
B2	0.238	9.47	-6.5731	<.0001***
B3	0.462	10.98	-6.4354	<.0001***
B7	0.826	12.49	-6.2855	<.0001***
B8	16.69	643.78	-6.5678	<.0001***
B9	0.797	12.97	-6.6588	<.0001***
B10	-	-	-	-
B11	10.63	331.36	-6.5248	<.0001***
B12	1.50	488.52	-6.7244	<.0001***
B13	1.26	68.92	-6.6207	<.0001***
B14	2.16	231.00	-6.6815	<.0001***
B15	0.349	50.37	-6.6982	<.0001***
B16	2.46	20.45	-5.8905	<.0001***
L1	0.774	46.95	-6.6328	<.0001***
L2	6.09	69.30	-6.1289	<.0001***
B12FS	1.14	170.41	-6.7011	<.0001***
L1FS	0.757	75.74	-6.6826	<.0001***

Appendix 8:

ZUBOVIC,STADNICHENKO AND SHEFFEY(1960)
[IN PERCENT]

SEAM ELEMENT	LIGHT FRACTION (X)	HEAVY FRACTION (Y)	Z-VALUE (Z)	TWO-SIDED PROBABILITY (P)
B	74.2	26.6	0.815	.4180
Be	94.0	7.2	1.24	.2150
Co	39.5	60.5	-0.392	.6966
Cr	41.9	58.1	-0.305	.7642
Cu	33.8	66.1	-0.589	.5552
Ga	58.6	42.7	0.296	.7718
Ge	65.3	37.1	0.506	.6170
Mo	38.7	61.3	-0.421	.3744
Ni	45.9	54.0	-0.154	.8808
Ti	62.0	38.7	0.430	.6672
V	59.2	41.9	0.321	.7490
Y	51.3	49.2	0.039	.9680
Zn	22.6	96.8	-1.01	.3174

Appendix 9:

MILLER (1977)
LIGNITE
[IN PARTS PER MILLION]

SEAM ELEMENT	LIGHT FRACTION (X)	HEAVY FRACTION (Y)	Z-VALUE (Z)	TWO-SIDED PROBABILITY (P)
Al	552.42	289.38	5.69	<.0001***
Ba	17.62	375.13	-12.841	<.0001***
Be	13.4	1.3	1.216	.2262
Ca	2787.88	897.41	8.707	<.0001***
Ce	81.0	70.0	0.139	.8886
Cr	110.0	26.0	1.00	.3174
Cu	13.02	2.27	10.97	<.0001***
Fe	457.3	2506.7	-10.851	<.0001***
K	59.93	48.89	1.927	.0536
La	26.0	20.0	0.246	.8026
Mg	743.0	53.4	12.487	<.0001***
Mn	7.31	49.33	-11.357	<.0001***
Na	734.11	51.2	12.518	<.0001***
Ni	62.0	35.0	0.511	.6110
Sr	58.49	15.72	9.541	<.0001***
Ti	43.58	14.69	8.483	<.0001***
V	96.0	28.0	0.917	.3628
Yb	17.0	6.0	0.823	.4122
Zn	12.981	0.07	12.981	<.0001***
Zr	266.0	83.0	0.886	.2788

Ely, F.G. and Barnhart, D.H. (1963) in Chemistry of coal utilization (H.H. Lowry, ed.), supp. v., p. 820-891, Wiley, New York.

Eskanazi, G. (1977) On the binding form of tungstem in coals: Chem. Geology, v. 19, pp. 153-159.

Finkelman, R.B., and Stanton, R.W. (1978) Identification and significa of accessory minerals from a bituminous coal: Fuel, v. 57, 1978., pp. 763-768.

Frondel, C. (1961) "The system of mineralogy of J.D. Dana and E.S. Dana", John Wiley and Sons, Inc., New York, 397pp.

Given, P.H., Spackman, W. Davis, A. Cronauer, D.C., Lovell, H.L., and Biswas, B. (1975) Dependence fo coal liquefaction behavior on coal characteristics, 1. vitrinite-rich samples; 2. role of petrographic composition: Fuel, v. 54, pp. 40.

Given, P.H., and Spackman, W. (1978) Reporting of analyses of low-rank coals on the dry, mineral-matter-free basis: Fuel, v. 57, p. 319.

Gluskoter, H.J. (1967) Clay minerals in Illinois coals: Jour. of Sed. Petrology, v. 37, pp. 205-214.

Gluskoter, H.J. (1975) Mineral matter and trace elements in coal: In "Trace Elements in Fuel", ed. S. P. Babu, Am. Chem. Soc. Advances Chemistry Ser. 141, Washington, D.C., pp.1-22.

Gluskoter, H.J. (1965) Electronic low temperature ashing of bituminous coal: Fuel, v. 44, pp. 285-291.

Gluskoter, H.J., Ruch, R.R., Muller, W.G., Cahill, R.A., Dreher, G.B., and Kuhn, J.K. (1977) Trace elements in coal: occurence distribution: Illinois Geol. Survey Circ. 499, 154 pp.

Gluskoter, H.J. and Lindahl, P.C. (1973) Cadmium: mode of occurence in Illinois coals: Science, v. 181, no. 4096, pp. 264-266.

Goldschmidt, V.M. (1950) Occurence of rare elements in coal ashes: "Progress in Coal Science", ed. P.H. Bangham, London, 238 pp.

Goldschmidt, V.M. (1954) "Geochemistry", Oxford.

Goldschmidt, V.M. (1930) The prescence of Ge in coal and coal products Nachr., Ges. Wiss., Gottingen, Math-phys., Klasse, Fach gruppe IV, pp. 398.

Goldschmidt, V.M. (1935) Rare elements in coal ashes: Indus. and Eng. Chem., v.27, no. 9, pp. 110-1102.

Govindaraju, K. (1980) Report on three GIT-IWG rock reference samples: anorthosite from Greenland, AN-G; Basalt d'Essey-la-Cote, BE-N; Granite de Beauvoir, MA-N, v. 4, no. 1, pp. 49-138.

Grim, R.E. (1968) "Clay Mineralogy", McGraw-Hill, New York, 569 pp.

Grim, R.E. and Kulbicki, G. (1961) Montmorillonite, high-temperature and classification: Am. Mineralogist, v.46, pp. 1329-1369.

Harder, H. (1959) Beitrag zur geochemie des bors, II-borin sedimenten: Akad. Wiss Gottingen Nachr. Math-Phys. Kl., v. 6, pp. 123-183.

Harder, H. (1961) Einbau von bor indetritesche tonminerale experimente zur eklarung des gorgehaltes toniger sedimente: Geochim. et cosmochim. acta, v. 21, pp. 284-294.

Hashimoto, S. (1953) Minor elements in coals from the Abrato coal mine, Yanagata Prefecture: Misc. Repts. Researh Inst. Nat. Resources, Japan, no. 31, pp. 27-34.

Hawley, J.E. (1955) Germanium content of some Nova Scotian coals: Econ. Geology, v. 50, no. 5, pp. 517-532.

Headlee, A.J.W. and Hunter, R.G. (1951) Germanium in coals of West Virginia: West Virginia Geol. and Econ. Survey, Rept. of Investigations, no. 8, pp.1-13.

Hendrix, S.B. (1942) Lattice structure of clay minerals and some properties of clays, J. Geology, v. 50, pp. 276-290.

Inagaki, M. (1951) Spectoscopic analysis of inorganic material in coal: Jour. of coal Research Institute (Japan), v.2, pp. 229-234.

Jedwals, J. (1960) Le charbon comme source de beryllium: Bull. Soc. Belge. Geol. Paleontol. Hydrol., v.69, pp.67.

Jeffrey, E.C. (1910) The nature of some supposed algal coal: Amer. Acad. Arts and Sciences Proc., v. 46, pp.273-290.

Jeffrey, E.C. (1915) The mode of origin of coal: Jour. Geology, v. 23, pp. 218-230.

Jenkins, R.G. and Walker, P.L. Jr. (1978) Analysis of mineral matter in coal and coal products: In "Analytical methods for coal and coal products, Vol. III", ed. C. Karr, Academic Press, New York ??pp.

Korolev, D.F. (1955) Technical problems connected with vanadium pentoxide: Brennstoff-Chem., v. 36, pp.151-155.

Krauskopf, K.B. (1967) "Introduction to geochemistry", McGraw-Hill, New York, 721 pp.

Kuhn, J.K., Fiene, F.L., Cahill, R.A., Gluksoter, H.J., and Shimp N.F. (1980) Abundance of trace and minor elements in organic and mineral fractions of coal: Envir. Geology Notes, no. 88, Illinois State Geol. Survey Division, Urbana, 67 pp.

Mackowsky, M.Th. (1968) Mineral matter in coal: In "Coal and coal bearing strata", ed. D.G. Murchison and T.S. Westoll, Oliver and Boyd Publishing Co., Edinburgh, pp. 309-321.

Maclean W.H. and Shimazake, H. (1976) The partition of Cobalt, nickel, copper and zinc between sulphide and silicate liquids: Econ. Geology, v.71, pp. 1049-1057.

Manskaya, S.M. and Drozdova, T.V. (1968) "Geochemistry of organic substances", ed. L. Shapiro and I.A. Breger, Pergamon Press, Oxford, 345 pp.

Marshall, C.E. (1935) Layer lattices and base-exchange clays: Z. Christ, v. 91, pp. 433-449.

Marshall, C.E. (1941) Note in the occurence and distribution of pyritic sulphur in coal: Min. and Pet. Tech. Mag., pp. 33-36.

Martell, A.F and Calvin M. (1952) "Chemistry of metal chelate compounds, Prentice Hall, New York, 613 pp.

Mason, B. and Berry, L.G. (1968) "Elements of Mineralogy", W.A. Freman and Company, San Francisco, 528 pp.

Miller, R.N. (1977) "A geochemical study of the inorganic constituents in some low-rank coals", Ph.D Thesis, The Pennsylvania State University.

Miller, R.N. and Given, P.H. (1978) Variations in organic constituents of some low-rank coals: In "Ash deposits corrosion, impurities and cobustile Gases, Proceedings of the International Conference, ed. R.W. Byers, pp. 39-50.

Mitchell, R.S. and Gluskoter, H.J. (1976) Mineralogy of ash of some American Coals: variations with temperature and source: Fuel, v. 55, pp.90-96.

Nankervis, J.C. and Furlong, R.B. (1980) Phase changes in mineral matter of North Dakota lignites caused by heating to 1200 degrees centigade: Fuel, v. 59, pp. 425-430.

Nicholls, G.D. (1968) Geochemistry of coal-bearing strata: In "Coal and coal bearing strata", Oliver and Boyd Publishing Co., Inc., ed. D. Murchison and T.S. Westoll, 418 pp.

Nicholls, G.D. and Loring, D.H. (1962) The geochemistry of some British Carboniferous sediments: Geochim. et Cosmochim. Acta, V. 26, pp. 181.

Ong, H.L. and Swanson, V.E. (1966) Asorption of copper by peat, lignite and bituminous coal: Econ. Geology, v. 61, pp. 1214-1231.

Otte, M.V. (1953) Spurenelemente in einigen deutschen steinkohlen. Chem. Erde., v. 16, no. 3, 239 pp.

Raiswell, R., Plant, J. (1980) The incorporation of trace elements into pyrite during diagenesis of black shales, Yorkshire, England: Econ. Geology, v. 75, pp.684-669.

Rao, C.P. and Gluskoter H.J. (1973) Occurence and distribution of minerals in Illinois Coals: Illinois State Geol. Surv. Circ., v. 476, 56 pp.

Ratinskii, V.M. (1946) Germanium in coal: Trudi Biogeochim. Lab, AN, U.S.S.R., v. 8, pp. 181.

Raymond, R. Jr. (1979) Relative abundances of common elements in coal macerals: Microbeam Analysis, ed. D.e. Newbury, San Francisco Press, California, 278pp.

Razdorozhnyy, V.F. (1968) Natural acidity of coals and its role in trace element accumulation processes: Geokyhimiya, v. 1, pp. 99-105. Translated in Geochemistry Translations v. 5, pp. 79-84.

Ruch, R.R, Gluskoter, H.J. and Shimp, N.F. (1974) Occurence and distribution of potentially volatile trace elements in coal-a final report: Illinois Geol. Survey Environmental Geology Notes 72, 96 pp.

Smyth, M. (1966) A siderite-pyrite association in Australian Coals: Fuel, v. 45, pp. 221-231.

Sprunk, G.C. and O'Donnell, H.J. (1942) Mineral matter in coal: U.S.Bur. Mines, Tech. Paper, v. 648, 67 pp.

Stach, E. (1968) Basic principles of coal petrology: macerals, microlithotypes and some effects of coalification: In "Coal and coal bearing strata", Oliver and Boyd, Edinburgh, pp. 3-17.

Stach, E. (1975) "Coal Petrology": Gebruder Borntraeger, Berlin, 428 pp.

Stadnichenko, T. (1934) Progressive regional metamorphism, Lower Kittanning Coal Bed, Pennsylvania: Econ. Geology, v. 29, pp. 511-543.

Stadnichenko, T., Murata, K.J. and Axelrod, J.M. (1950) Germaniferous lignite from the District of Columbia and vicinity: Science, v. 112, p 109.

Stadnichenko, T., Murata, K.J., Zubovic, P. and Hufschmidt, E.C. (1953) Concentration of germanium in the ash of American Coals: U.S. Geol. Survey Circ., v. 272, 34 pp.

Stadnichenko, T., Zubovic, P. and Sheffey, N.B. (1961) Beryllium content of American coals: U.S. Geol. Survey Bull., v. 1084-k, pp. 253-295.

Szalay, A. (1957) The role of humus in the geochemical enrichment of uranium in coal and other bioliths: Acta Phys. Acad. Hung., v. 8, pp. 25-36.

Szava, Benocs K, (1966) Dunantuli szentelepek ritkafem katasztere: Kutatasi reszjelentes, 1-26-66-1051b, BKI, Budapest.

Szilagyi, M. (1971) The role of organic matterin the distribution of Mo, V, and Cr in coal fields: Econ. Geology, v. 66, pp. 1075-1078.

Valeska, F, Malan, O. and Kessler, M.F. (1967) Bonding of some micro elements in coal: Vysledky Banskeho Vysk. v. 5, pp. 212-218.

Van Krevelen, D.W. (1961) "Coal": American Elsevier Co., Inc., New York, 323 pp.

Voskresenskaya, N.T. (1968) Thallium in coal: Geokhimiya, no. 2 pp. 207-216, Translation in Geochemistry translations, v. 5, pp. 158-167.

Walpole, R.E. and Myers, R.H. (1978) Probability and statistics for engineers and scientists: 2nd edition, MacMillan Publishing Co., Inc., 580 pp.

Watt, J.D. (1968) The physical and chemical behavior of the mineral matter in coal under conditions met in combustion plants, part 1, B.C.U.R.A., Leatherhead, England.

Weaver, C.E. and Pollard, L.D. (1975) "The chemistry of clay minerals": Elsevier Scientific Publishing Co., Inc., New York, 213 pp.

Wedepohl, ed. (1969-1974) "Handbook of Geochemistry": Elsevier Publishing Co.. New York.

Zubovic, P., (1966a) Physico-chemical properties of certain minor elements as controlling factors in their distribution in coal: In "Coal Science", ed. R.F. Gould, Am. Chem. Soc., Washington, D.C., pp.221-231.

Zubovic, P. (1966b) Minor element distribution in coal samples of the Interior Coal Province: In "Coal Science", Ed. P. Given, Am. Chem. Series 35, 243 pp.

Zubovic, P. (1976) Geochemistry of trace elements: In "Symposium proceedings: Envir. aspects of fuel conv. tech., II, ed. F.A. Ayer, U.S. Envir. Prot. Agency, Envir. Prot. Technology Series, EPA-600/2-76-149, pp. 47-63.

Zubovic, P., Stadnichenko, T. and Sheffey, N.B. (1960) The associations of some minor elements with organic and inorganic phases of coal: U.S. Geol. Survey, Prof. Paper, v. 400-B, pp. B84-B87.

Zubovic, P., Sheffey, N.B., Stadnichenko, T.M. (1961) Chemical basis of minor-element associations in coal and otner carbonaceous sediments: U.S. Geol. Survey, Prof. Paper, v. 424-D, pp. D345-D348.

Zubovic, P., Stadnichenko, T. and Sheffey, N.B. (1961) Geochemistry of minor elements in coals of the Northern Great Plains Coal Province: U>S. Geol. Survey Bull. v. 1117-A, 58 pp.