DISTRIBUTION OF FERROUS IRON AMONG THE ORGANIC HYDROCARBONS, NON-PYRITIC INORGANIC MINERAL CONSTITUENTS AND PYRITE FRACTION OF TWENTY COALS FROM NEW MEXICO, NOVA SCOTIA, AND WESTERN KENTUCKY

by

Patricia A. Cooksey

Submitted in Partial Fulfillment
of the Requirements for the Degree of
Master of Science in Geology

New Mexico Institute of Mining & Technology
Socorro, New Mexico
Oct, 1980

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ABSTRACT

A series of chemical extractions were used to determine distribution of ferrous iron among the organic hydrocarbons, non-pyritic inorganic mineral constituents and pyrite fraction of twenty coals from New Mexico, Nova Scotia, and western Kentucky. Distribution coefficients for iron among the cited fractions were calculated. Distribution coefficients and iron concentrations within specified coal fractions were compared to percent fixed carbon (dmmf) in order to determine correlations which would indicate rank dependency. These values were also compared to percent mineral matter. Relationships were observed between percent mineral matter and (1) distribution coefficients, (2) the organic iron concentration within the hydrocarbon fraction, (3) the carbonate iron concentration within the non-pyritic inorganic coal fraction, and (4) the pyrite fraction. The correlations ranged from mild to strong. No significant relationship was found between distribution coefficients or iron concentrations and fixed carbon content (dmmf). This occurrence was thought to reflect the narrow range of the carbon content of the samples studied, the lack of separation of constituents in analyses, or the non-equilibrium state of the iron distribution in the coal specimens.

Distribution coefficients were calculated from sample data published by the Illinois State Geological Survey (Gluskoter, et al., 1980). The values were plotted against percent fixed carbon (dmmf) and percent mineral matter. No relationship was found

between fixed (dmmf) carbon and the distribution coefficients. A mild relationship appeared between percent mineral matter and the distribution coefficients.

It was concluded that there appears to be a mild relationship between distribution coefficients and percent mineral matter but that there is no dependency of distribution coefficients upon rank.

ACKNOWLEDGMENTS

The author would like to thank Dr. Frederick J. Kuellmer for suggesting this investigation and for his guidance and encouragement. This study was made possible by support from the New Mexico Mining and Mineral Resources Research Institute under support from the Office of Surface Mining, Department of the Interior, Grant G5114031. A special sense of gratitude and indebtedness is owed Mrs. Lynn Brandvold and the New Mexico Bureau of Mines and Mineral Resources for use of laboratory equipment and facilities. Added appreciation is expressed to Mrs. Brandvold for her unending patience, helpful suggestions and guidance concerning laboratory procedures. The author would like to thank Frank Campbell (New Mexico Bureau of Mines and Mineral Resources) for proximate analyses performed and Ms. Nancy Blount for doing the analytical work. Also my gratitude to Dr. Renault and Ms. Babette Faris for help extended in the examination of whole coal samples by x-ray diffraction. Lastly, thanks to Ms. Jill Evensizer for helpful suggestions concerning the writing of this paper.

STATEMENT OF PROBLEM

This investigation measured the distribution of iron among selected geochemical phases in twenty coals from New Mexico (17), Nova Scotia (2), and western Kentucky (1), in order to see if there is a regular distribution of iron among the organic hydrocarbons, non-pyritic inorganic mineral constituents, and pyrite fraction. Iron was separated from the following geochemical phases: (1) exchangeable, (2) carbonate, (3) iron oxide, (4) hydrocarbon, and (5) pyrite. Percent pyrite was determined from the extracted pyritic iron. Measurement of these iron contents permitted calculation of distribution coefficients which were then compared to fixed carbon (dmmf) and percent mineral matter in order to seek correlative relationships. Such relationships would suggest a tendency towards a physico-chemical equilibrium following the initial coalification. If this were the case, distribution coefficients might be useful to quantify pressure, temperature and time parameters during coalification. Environmentally, this study separated and measured the amount of iron which is: (1) readily soluble (exchangeable); (2) released during hydrocarbon oxidation (organically bound); and (3) locked within crystal lattices of (a) oxides, (b) carbonates, or (c) pyrite. Selected iron concentrations were plotted against percent mineral matter and fixed carbon (dmmf) and the plots examined for correlative relationships.

IRON GEOCHEMISTRY

Iron is an abundant lithospheric element, ranking fourth in mass abundance behind oxygen, silicon , and aluminum. Iron occurs within coal as: (1) primary allogenic minerals deposited in the coal swamp; (2) syngenetic inorganic mineral species precipitated from or deposited by an aqueous medium during peatification or earlier; (3) epigenetic mineral species either diagenetically derived or deposited by ascending or descending solutions in cracks and fissures formed during solidification of the coal gel; and (4) metallo-organic complexes, considered to be most prevalent in low-rank coals (Spirro and Kosky 1982; Stach, 1980; Zobovic et al.,1961, and Fowkes, 1978).

Although syngenetic iron-bearing mineral matter can form partings within the coal, it is generally considered to be more evenly distributed, finer and more difficult to separate from organic material than is the epigenetic matter. The term "mineral matter" refers only to inorganic matter which does not include any metallo-organic complexes. Because of this limitation, coal ash has two components: (1) adventitious ash due to allochthonous mineral matter; and (2) inherent ash due to inorganic material formed from original plant material after the death of the plant. High temperature ash content is not equivalent to mineral matter content because the original minerals are altered due to oxidation and volatization during combustion.

The following major mineral groups make up the mineral matter in coal: clays, sulfides and sulfates, carbonates, oxides, silicates, phosphates and accessory minerals (Gluskoter et al., 1977; MacKowsky, 1968; Stach et al., 1982; Ergun, 1979; and O'Gorman and Walker, 1972). Gluskoter et al., (1977) state that the majority of coal minerals are in one of four groups: clays, carbonates, sulfides and quartz. Pyrite (FeS_2, cubic) is the dominant sulfide although its dimorph marcasite (FeS_2, orthorhombic) can occur (Kuhn et al., 1980; Gluskoter et al. 1977). In Gluskoter's opinion, iron sulfate present in coal is most likely the result of pyrite oxidation which, he concludes, can occur at room temperature. Although siderite ($FeCO_3$) has been reported in mineralogical studies of coal, ankerite ($2CaCO_3MgCO_3FeCO_3$) is the most frequently reported iron carbonate. Montana, (1980), measured the distribution of iron-bearing minerals in coal using Mossbauer spectroscopy, finding (in order of abundance) pyrite, marcasite, clays (illite), sulfates, carbonates, and others (less than 0.1%).

Eventhough iron is considered to have an inorganic affinity, (Gluskoter, 1980), iron must also be associated with the hydrocarbon fraction of coal. This results from the inclusion of trace amounts of iron within the biosphere due to the involvement of iron in such physiological processes as electron transport during chlorophyll production, oxygen transport or respiration, and fermentation. Iron is considered to be a highly versatile biocatalytic agent because of its two valence states (Fe2+ and

Fe3+) and the wide range of oxidation-reduction potentials of various iron-containing compounds during ferrous-ferric transitions (Lundgren and Dean, 1980). Figure 1 (p. 213, ibid.) shows the movement of iron through the biosphere and its availability to bioforms. The following points summarize Lundgren's and Dean's discussion of this cycle.

1. Organic iron requirements are supplied from inorganic iron reservoirs.
2. Constant iron movement occurs from terrestrial reservoir to hydrosphere sink where it is available for use by organisms.
3. Oceans contain only about 3 ug Fe/l (fresh bodies of water slightly more). This limited amount and the large iron reservoirs indicate that iron begins to precipitate and settle upon entering the hydrosphere. Its form depends upon environmental conditions.
4. Organic complexes may be more energetically stable than non-organic hydrated species.
5. Both hydrated iron species and metallo-organic complexes may be absorbed or adsorbed by clays or humus depending upon complex environmental considerations.

Zobovic, Stadnichenko, and Sheffey (1961), correlated organic affinity with properties most likely to affect formation and stability of metallo-organic complexes. These properties are size and charge of ion, bond configuration and coordination number, tendency to form covalent instead of ionic bonds and degree to which the metal combines with the nitrogen rather than

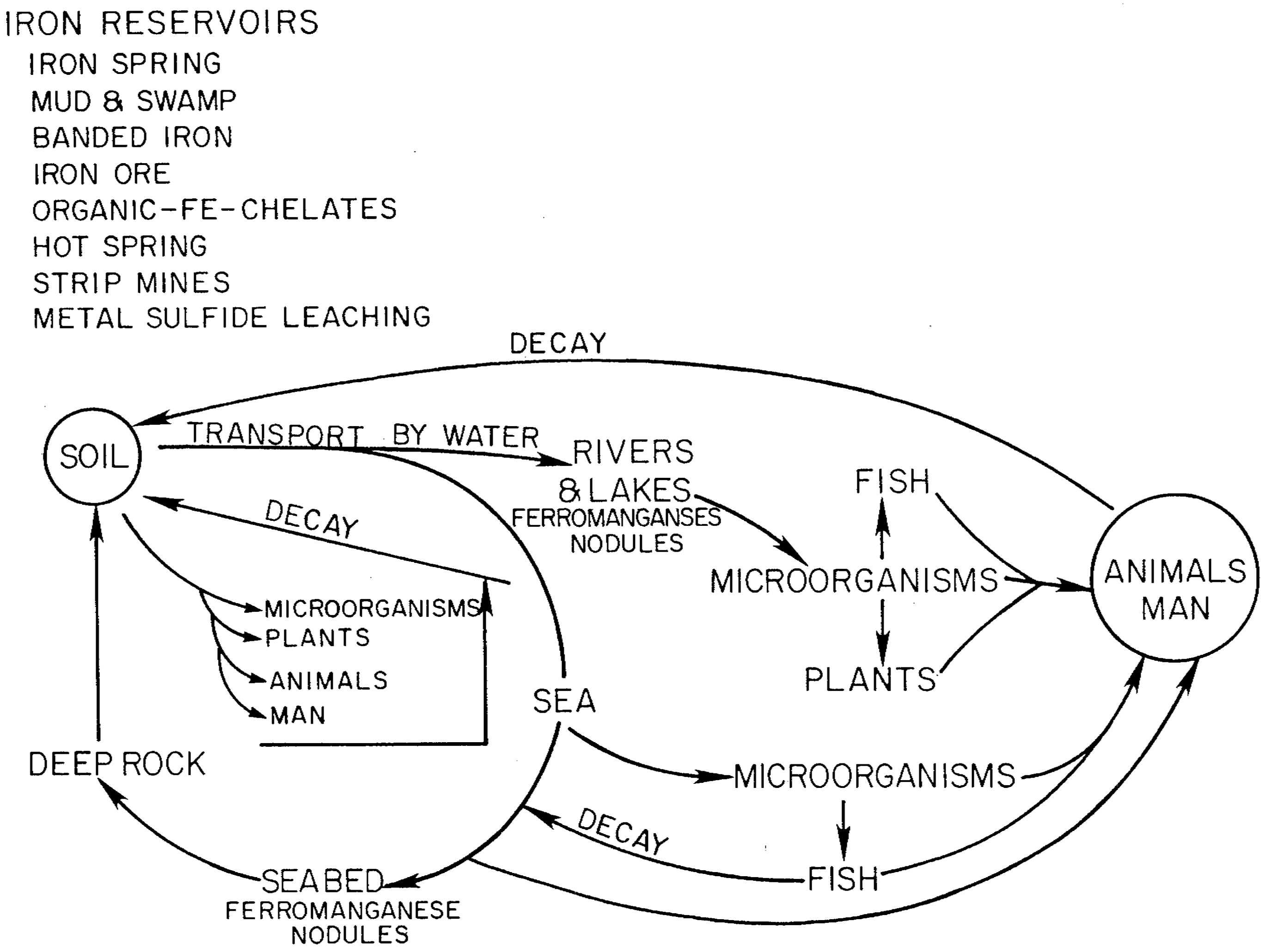

Figure 1: Movement of Iron through the biosphere and its availability to microoganisms, plants and animals. (Source; Lundgren and Dean, 1980)

with the oxygen or sulfur of the donor molecule. Selected bivalent metallo-organic complexes of iron were shown to be less stable than metallo-organic complexes of cobalt, nickel or copper due to the size to charge ratio of the bivalent iron ion. Small size and high charge increase the likelihood of forming a stable complex.

Breger (1958) summarizes (in Bouska, 1981) data on the geochemical effects of organisms on trace element accumulation. This summary shows that iron can accumulate biogenetically due to life processes of organisms as well as chemically after the organism's death as inorganic sulfides by means of complex physico-chemical processes.

Bouska further reports that Czech researchers, Kudelasek (1959) and Suasta et al. (1955), studied trace element accumulation in coal. Germane to iron accumulation is the conclusion stating the dependence of elemental species in coal on the coal facies i.e. maceral content, and the pH-Eh environment during peat formation and early coalification. Cited is the fact that changes in Eh affect both the origin of the coal maceral and the accumulation or dispersion of trace elements by either increasing the element's solubility (dispersion and perhaps loss from the system) or decreasing its solubility (accumulation by precipitation). These Eh controlled oxidation-reduction processes are influenced in turn by pH values and ionic activities of the species involved. Figure 2 shows generally accepted pH-Eh boundaries, inorganic iron species distribution, and optimum pH-Eh conditions for siderophillic organisms (Lundgren and Dean, 1979).

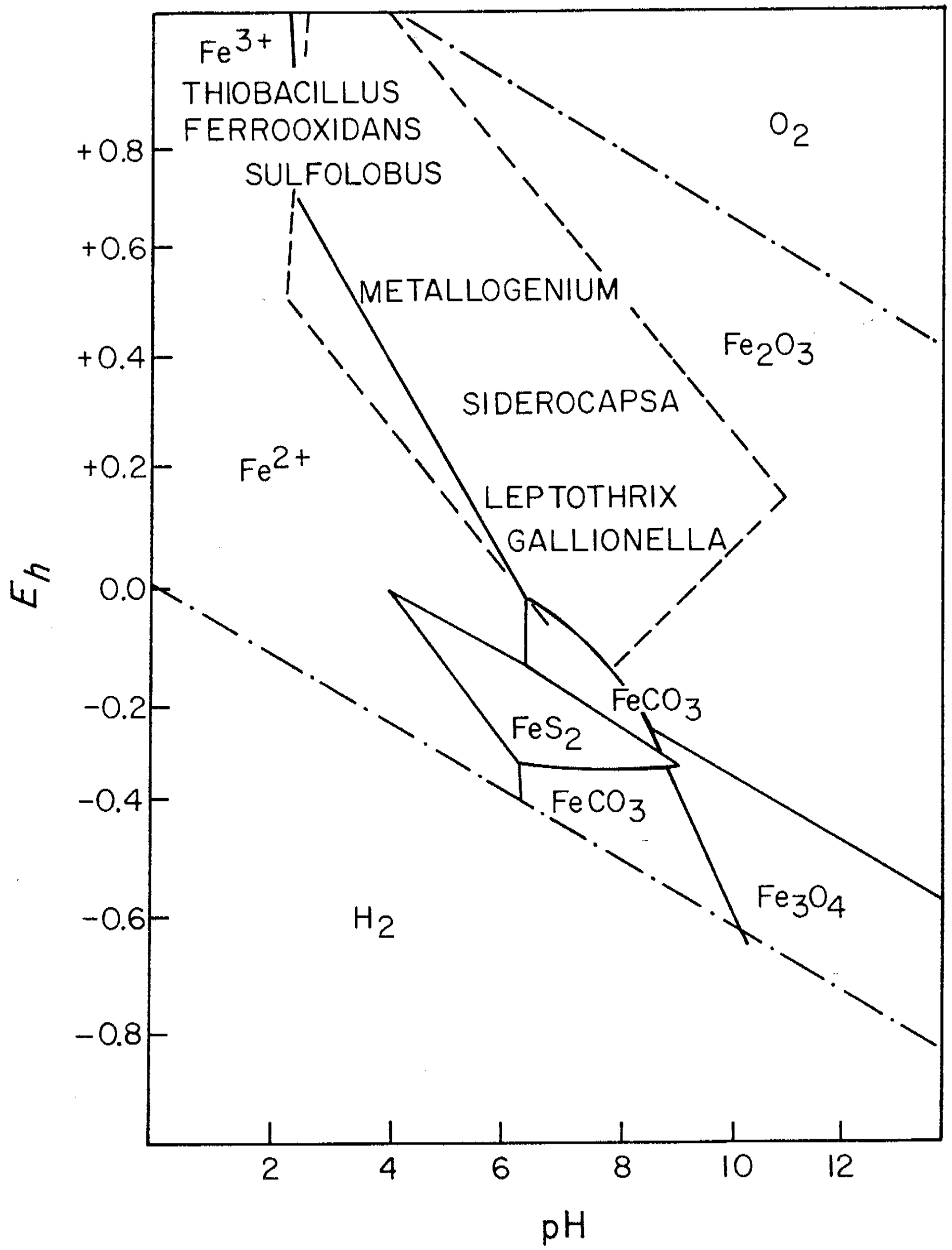

Figure 2: Eh/ph iron stability diagram. Natural domains of the main groups of the iron bacteria are shown. (Source: Lundgren and Dean, 1980)

Zubovic et al. (1961) discussed the elemental associations with organic material and concluded the following.

1. Elements are partitioned between organic and inorganic phases during peatification (gel period).
2. Peat bogs afford environments wherein hydrogen sulfide (H2S) forms due to bacterial activity. The sulfide ion is the stable oxidation state for sulfur (refer to Figure 2) in this environment.
3. Relationships exist between the stability of some of the organic complexes and possible inorganic phases. For example, general stability of organic complexes of bivalent metals is Be 2+ > Cu 2+ > Ni 2+ > Co 2+ > Zn 2+ > Fe 2+; however, in an extremely acid environment, suffides are not stable leading to preferential formation of organic complexes. As neutrality is reached, sulfides will begin to precipitate since this form is now favored.
4. Such relationships as described under item (3) can be altered by the organic/metallic ion ratio. A high ratio favors metallo-organic complexing and a low ratio formation of an inorganic phase.

Parameters governing iron sulfide formation are complex. A simplified summary of the steps involved follows: (1) hydrogen sulfide forms due to bacterial reduction of sulfate or decomposition of sulfur-containing organic compounds; (2) hydrogen sulfide reacts with iron to form FeS (mackinawite) or Fe_3S_4 (greigite) which are amorphous at precipitation; (3) added hydrogen sulfide production and the presence of sulfur oxidizing bacteria leads to elemental sulfur production which makes possible the precipitation of pyrite (Berner, 1970).

Theis and Singer (1975) state that metallo-organic compounds can form after the death of a plant in the presence of oxygen if significant concentrations of organic matter are present. Ordinarily at pH (approximately) 7 iron is oxidized to ferric iron which precipitates as insoluble iron hydroxide (Fe(OH)3). Carbon is a reducing agent. Its presence may result in the formation of Fe 2+. When a large amount of organic matter is present, metal complexing may compete with the oxygenation. The rate of iron metallo-organic formation depends on the pH of the environment as well as on the type of organic matter present. Leaves contain the most iron, woody material the least. Humic acid present can either help fix the metallo-organic molecules within a soil or promote iron dissolution (Aristovskaya and Zavarzin, 1971).

Fowkes,(1978), Stach, (1980), and Zobovic, (1961), while examining mineral content of coal macerals found older and more highly metamorphosed coals to contain less organically bound inorganic elements than the less metamorphosed coals (lignites) and believe that this reflects a decrease in coordination and direct ionic bonding sites as well as decreased coal permeability which forces water along cleats where mineralization occurs rather than throughout the coal matrix.

Senesi et al. (in Bouska, 1980), studied the oxidation state and position of iron bound to humic and fulvic acid using electron spin resonance and Mossbauer spectroscopy and found iron to be trivalent (Fe3+). They concluded that if ferric iron is bound by tetrahedral and octahedral coordination, it is resistant to complexing and reduction. On the other hand if the ferric iron is only adsorbed, it is easily complexed and reduced (Fe2+).

Researchers conclude that iron concentration depends upon the plant community and type of plant part preserved as well as on the depositional environment.

EXPERIMENTAL

Introduction

The premise behind any sequential extraction process is that it is possible to dissolve one species (inorganic or organic) without affecting others if a reagent can be found which is specific for that particular species. Geochemists have developed an array of such procedures in answering diverse chemical questions involving sediments in all types of environments. Kaplan, Emery and Rittenberg (1963); Chester and

Hughes (1967); Chester and Messiha-Hanna (1970); Anderson and Jenne (1970); Smith and Bates (1974); Zobovic (1966); Zobovic, Stadnichenko, and Sheffey (1960, 1961); Presley, Kolodny, Nissenbaum and Kaplan (1972); Gibbs (1977); Casagrande, Siefert, Berschinski, and Sutton (1977); Casagrande and Erchull (1976); Gupta and Chen (1975); Tessier, Campbell and Bisson (1979); and others have reported studies based upon some type of sequential extraction. Casagrande's studies involved the sequential extraction of iron (and other elements) from major hydrocarbon fractions as well as total metal for various levels within peat of the Okephenokee Swamp, Georgia. Presley et al. (1972) determined elemental speciation (including iron) within a sulfide-rich reducing environment (Saanich Inlet, British Columbia). Because these studies (and others) have successfully used sequential extractions for speciation between geochemical phases in reducing environments high in organic content, extension of these methods to coal does not seem unreasonable.

The procedure selected for this study is based upon one used by Tessier, Campbell and Bisson (1979) which in turn was adapted from a procedure reported by Gupta and Chen (1975). The inorganic geochemical phases i.e. exchangeable clay, carbonate, iron-oxide, and pyritic which are extracted all parallel dominant inorganic mineral species found in coal. As will be seen in the succeeding section, organic iron is not determined using floated fractions or demineralized coal as done by other workers (Gluskoter et al. 1977) but is evaluated by oxidizing the whole coal sample.

Sample Distribution and Description

Pertinent information regarding the coals studied i.e., sample designation, location (county, township and range, if known), type of sample, age and geologic formation, if known, are given in the table of Appendix 1. Raton Basin samples (16727-6 and 16815-1) and the west Kentucky, Mulford coal (16815-2) are composite samples. The coals range in fixed carbon values from 37.9 to 58.78%; in ash values from 3.6 to 23.1%; in moisture from 0.19 to 13.9%; and in sulfur from 0.36 to 3.52%. As received proximate analyses and fixed carbon (dmmf) values are listed in Appendix 2A.

Sample Preparation

All samples were sealed at the collection site in heavy polyethylene bags to minimize oxidation. Individual samples were crushed until all material would pass a 20 mesh sieve. The sample was then reduced to approximately 10 grams by coning and quartering. Each 10 gram sample was further pulverized for 3 minutes under liquid nitrogen (boiling point - 195.8 C) in a cryogenic grinder (Spex Freezer Mill) making sure that adequate space was left in the polycarbonate tube to insure complete pulverization by the steel grinding rod. Samples were pre-cooled in liquid nitrogen to guarantee that they were at ambient grinder temperature during the grinding episode. The ground sample was put into a 40 mm. plastic pill bottle, labled, sealed and placed in a desiccator to await treatment.

Sample numbers C-7, DT519772, DT519771, 16727-6, 16727-2, NM-TM, C 86 D, K 1-5, K 2-5, C 87 D, C 82 DW, and C 88 D were ground (inside a plastic bag) using an agate mortar and pestle until all material passed a 325 mesh sieve. Samples were dried under vacuum at ambient room temperature to constant weight prior to beginning the sequential procedure.

Procedure

X-ray diffraction of the whole coal was done on a diffractometer using CuK radiation (1.542 A). The KV and mV settings were 40 and 20 respectively. Entrance slits were 1.0mm; exit slits 0.3mm. Prepared samples were packed into metal frames and x-rayed. Settings used in the study are listed in Appendix 3.

Figure 3 illustrates the general sequential extraction procedure used for this study. Additional details are given in Appendix 4A and Appendix 4B. Time and reagent parameters were checked by subjecting NBS Standard Reference Material 1635 (Trace Elements in Coal), to the sequential partitioning process under varying experimental conditions and evaluating the amount of iron extracted.

Any treatment not requiring heat was carried out in a centrifuge tube fitted with a plastic cap. Supernatant solution and solid material were separated by centrifuging (Sorvall RC-5B

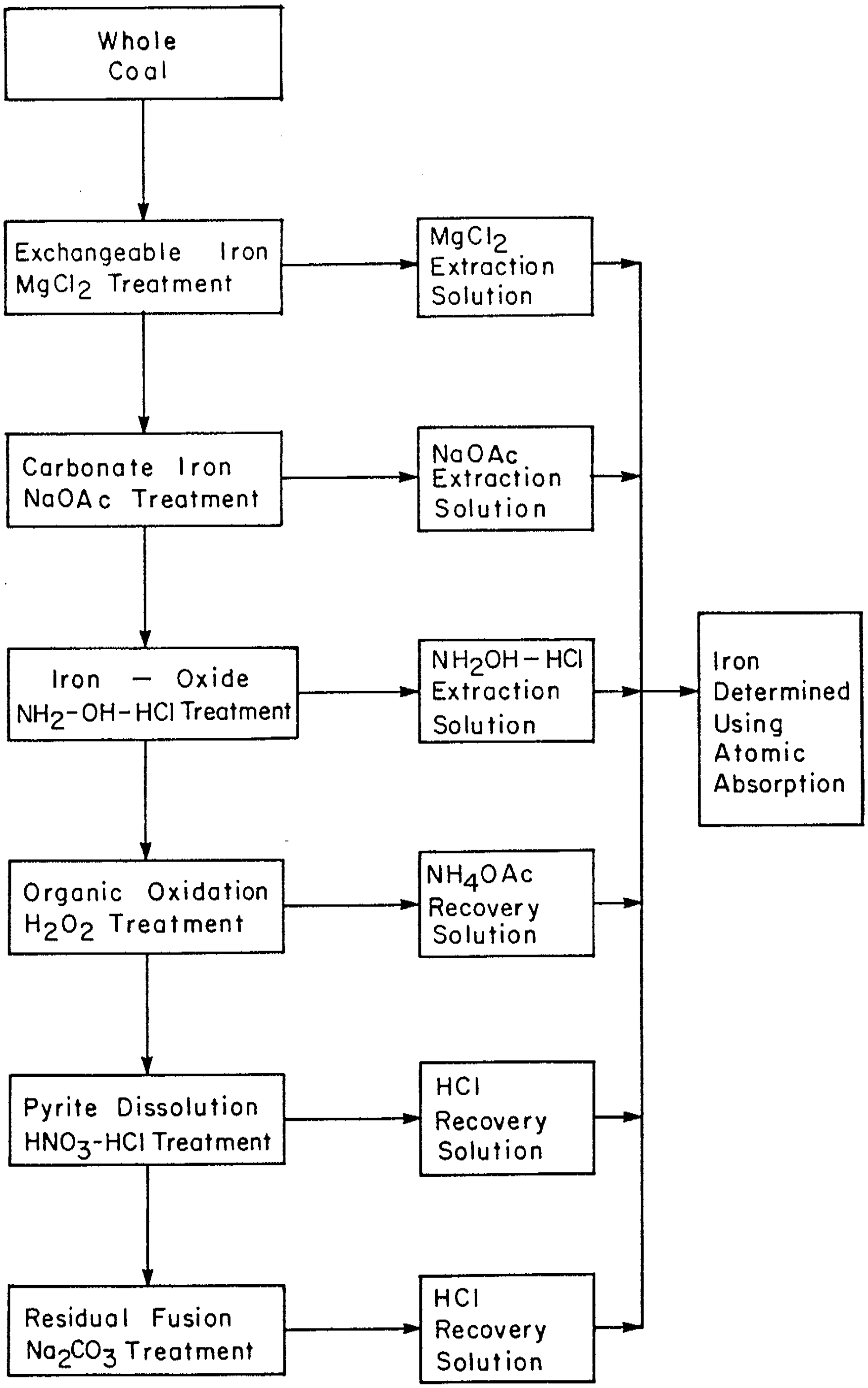

Figure 3: Sequential Extraction Procedure

Refrigerated Superspeed Centrifuge) at 12000 rpm (revolutions per minute) for 30 minutes. The solution was decanted through Whatman number 5 filter paper. Particulate matter caught in the filter paper was rinsed back into the centrifuge tube using 10 ml deionized water which served as rinse water. This mixture was centrifuged and decanted as described above and the rinse water discarded. Particulate matter remain- ing on the filter paper after decantation was washed into the appropriate tube using a measured amount of the next extracting solution. Each supernatant solution was stored in a 40 mm. amber pill bottle fitted with a snap cap. Iron was determined with the Varian Techtron, model 1250, using standard atomic absorption methods. The burner was positioned 7 cm above the light path. A strongly oxidizing air-acetylene flame was used. The slit opening was 0.2mm. Absorption was determined at 2483 angstroms. The settings used were those suggested by the manufacturer. Appropriate solutions were used for zeroing the instrument before determining absorption. Standard curves were drawn after each run. If the curves were non-linear, new standards were prepared (using appropriate reagents) and iron absorption redetermined. Special blanks were run for procedures 4, 5, and 6. Agitation was produced by a Burrell wrist-action shaker. Chemicals used in the experiment were reagent grade. Solutions were made with deionized water from research Model 1 IonXchanger (Illinois Water Treatment Company). Glassware was rinsed twice in 10% hydrochloric acid before being rinsed with deionized water.

Precision and Accuracy

Accuracy of the amount of iron extracted was evaluated by sequentially extracting iron from two series of triplicate samples of NBS Standard Reference Material 1635 (Trace Elements in Coal) which has a certified total iron value of .239+-.005 weight percent. The mean total iron extracted from the five geochemical phases for the first series was .2618 (+-9%) weight percent and for the second triplicate, .2272 (+-9%) weight percent. The first value is within 9% of the certified total iron value and the second 5%. The accuracy of these values is similar to those reported for a sequential extraction study by Tessier et al. (1979), who compared summed fractional metal content to total metal.

Precision varied for individual phases. Standard deviations are listed in Appendix 6A. Standard deviations for exchangeable, carbonate, and iron oxide geochemical phases range from 0.2 to 21 percent with an average value of 5.4 percent. The mean standard deviation was greatest (21%) for the organic fraction. This value reflects rapid oxidation of some samples which may have caused loss of material, as well as, occasional formation of refractory carbon which may have terminated iron release. Presley, Kolodny, Nissenbaum and Kaplan, 1972, reported "minor" problems with hydrogen peroxide oxidation of organic rich black shales but did not elaborate. Mean standard deviation for the pyritic fraction is 10 percent.

The detection limit for the Varian Techtron, model 1250, is 2 ug/l or 2 parts per million. The lowest level of iron detected was 11 parts per million which is well above the cited limit.

Obviously, the reproducibility of results for the sequential extraction of iron (or any other element) from coal has not been thoroughly tested due to time considerations, for many repetitions are necessary to define the extent of reproducibility as well as refine experimental parameters; however, the work on NBS Standard Reference Material 1635 (Trace Elements in Coal) seems to indicate that the result can be reproduced to within 10 percent (summed total iron).

Particle size and temperature may influence accuracy and precision. The less than 325 mesh particle size accompanied by low coal density (approximately 1.2) makes separation of supernatant solution difficult without loss of material. It is possible that a larger particle size would reduce this problem. However, the particle size should not be greater than 80 mesh. Agemian and Chau (1976) report that Oliver (1973) showed size affects extractability of metal and that Hawkes and Webb (1962) determined that the mesh size must be less than 80 mesh for extractions to be effective. These researchers recommend that material be ground to pass a 200 mesh screen for total metallic recovery. The smaller particle size would be more easily oxidized during the oxidation of the hydrocarbon fraction. The cause of refractory carbon formation during oxidation is not known. It may possibly form as a result of rapid oxidation which ends in flame production or an over-heating of the 30% hydrogen peroxide due to unequal heat distribution on the hot plate.

Results

Only one mineral was positively identified by x-ray diffraction of whole coal samples. This mineral is quartz. Clay peaks appear (e. g. kaolinite, montmorillinite and smectite) which indicate the presence of clay mixtures which differ in kind and amount among the various coals. Pyrite, iron oxide, and carbonate species cannot be identified from the X-ray diffraction charts. However,this is consistent with the small weight percent of iron recovered compared to the weight percent of ash. Peak interference and hydrocarbon dilution may contribute to identification difficulties.

Raw data for each geochemical phase, along with appropriate standard curve values are presented in the table of Appendix 5: Parts A through F. Concentration in parts per million for each sample was calculated using the following relationship:

$$\underset{\text{(ppm)}}{\text{Iron}} = \frac{\text{sample volume} \times \text{sample absorption} \times \text{standard concentration}}{\text{standard absorption} \times \text{sample weight in grams}}$$

Appendix 6A, lists mean iron concentration and standard deviation for each triplicate sample for the five geochemical phases. Concentrations are given in parts per million. To facilitate discussion, Appendix 6B lists the iron concentrations for each geochemical phase as a percent of the total iron content. Figures 4 through 8 are histograms representing these percentages. Table 1 identifies the samples as represented on the histograms.

Exchangeable iron, considered to be any extracted iron ions coming from exchange sites on clays or be due to carbon adsorption, was detected in the exchangeable leachate of five samples i.e. samples 16815-2, C 86 D, K 1-5, C 84 DD, and C 82 DW. With the exception of sample 16815-2, (Mulford coal composite from west Kentucky), which contained 31%, no more than 6 % of the total iron recovered appears to be exchangeable iron.

Between 0.1 to 3% of the total iron content was detected in the carbonate fraction of seven samples (DT5199772, 16727-6, NM-TM, 16815-2, 16815-1, C 86 D and C 87 D).

All samples contained measurable amounts of iron bound to the iron oxide component. Content range is from 2 to 22% with a mean of 9.5 percent. The mean value for iron associated with the organic hydrocarbon fraction is 5.5% (range from 2 to 12%) of the detected iron. Iron values for the pyritic fraction range from 64 to 95%, having a mean of 83 percent. Weight percent pyrite (whole coal basis) calculated from the experimental pyritic iron values are up to ten times greater than the mean pyrite content determined using forms of sulfur data reported by Pillmore

Table 1: Sample Identification List for Histograms 4 through 9*

Histogram Number	Sample Identification
1	DT519772
2	DT519771
3	16727-6
4	16727-2
5	NM - TM
6	16727-1
7	DT419771
8	16727-5
9	16815-2
10	16815-1
11	C - 7
12	16727-3
13	418771B
14	C 86 D
15	K 1 - 5
16	K 2 - 5
17	C 87 D
18	C 84 DD
19	C 82 DW
20	C 88 D

* The sample number corresponding to the column showing the magnitude of the measurement is at the right-hand edge of the column in figures 4 to 9, inclusive.

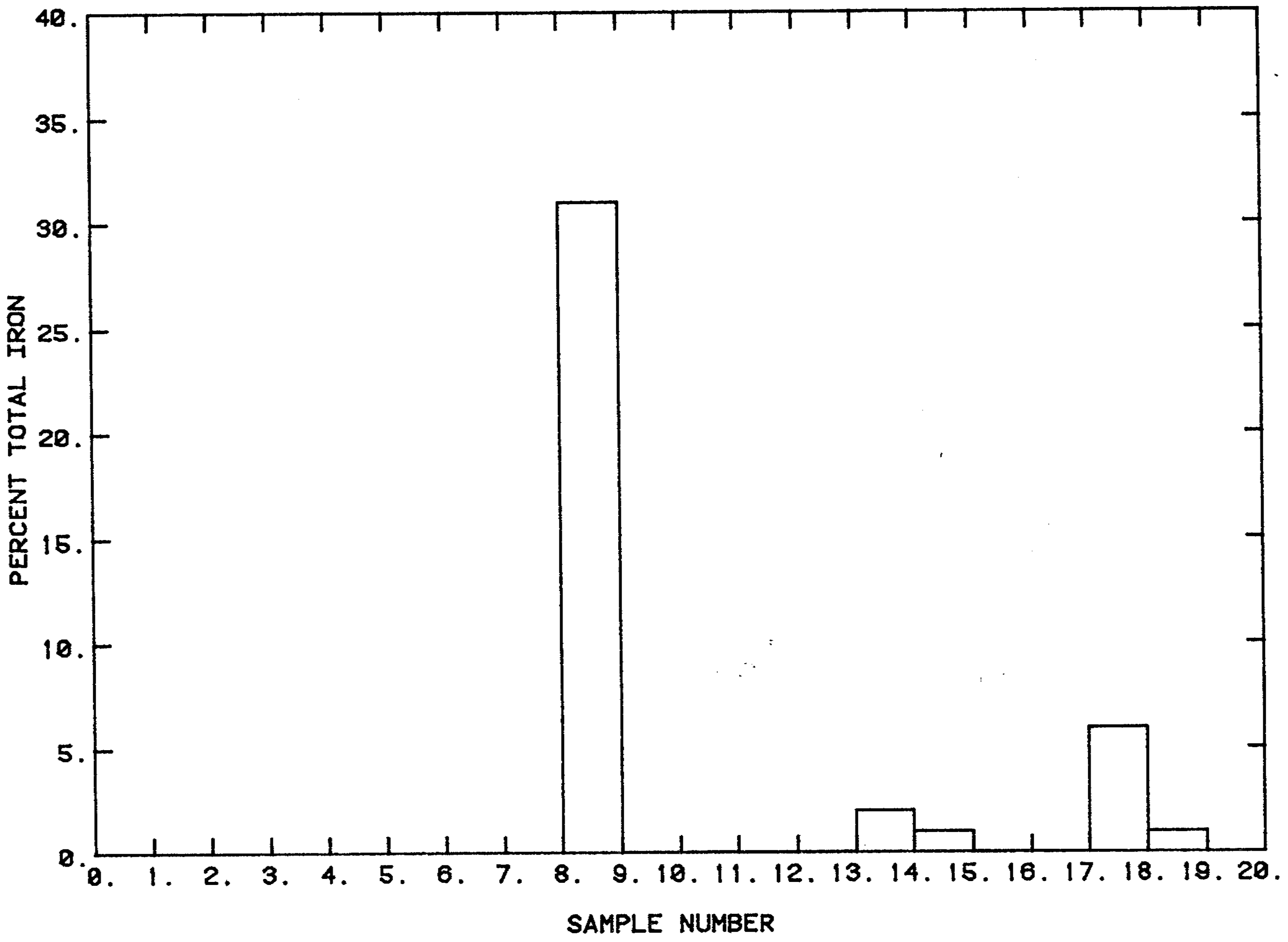

Figure 4. Percent total iron recovered from the exchangeable geochemical phase.

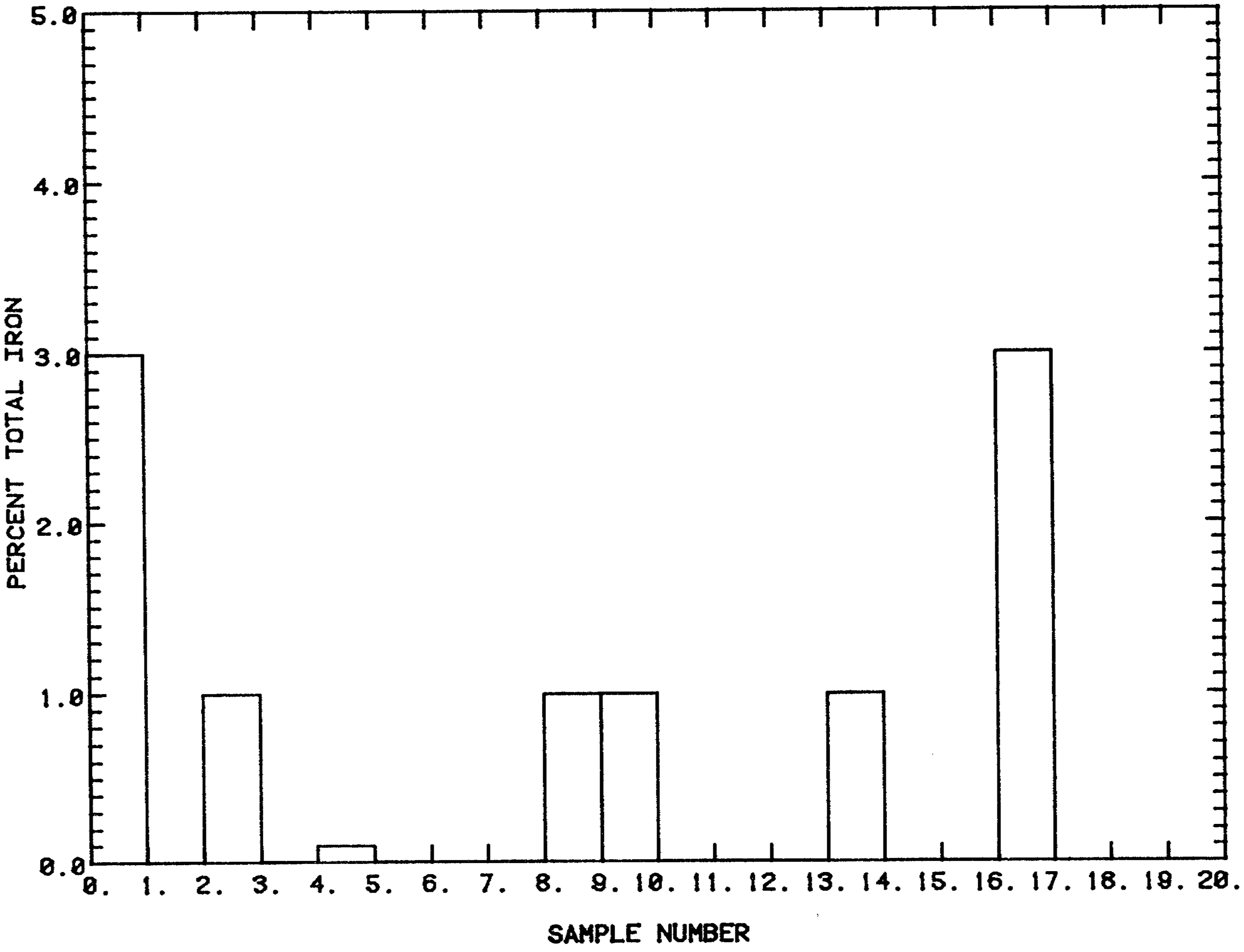

Figure 5. Percent total iron recovered from the carbonate geochemical phase.

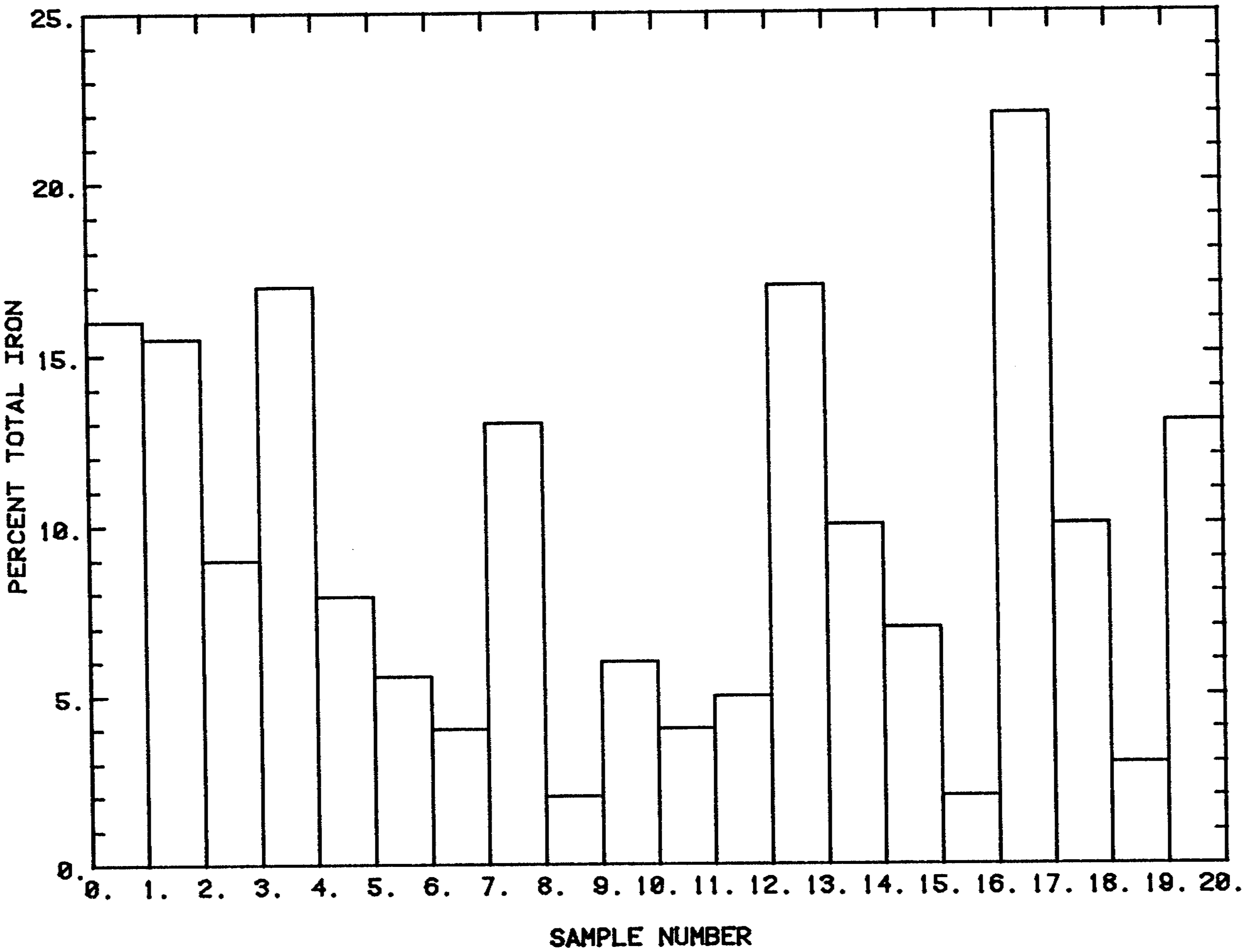

Figure 6. Percent total iron recovered from the iron oxide geochemical phase.

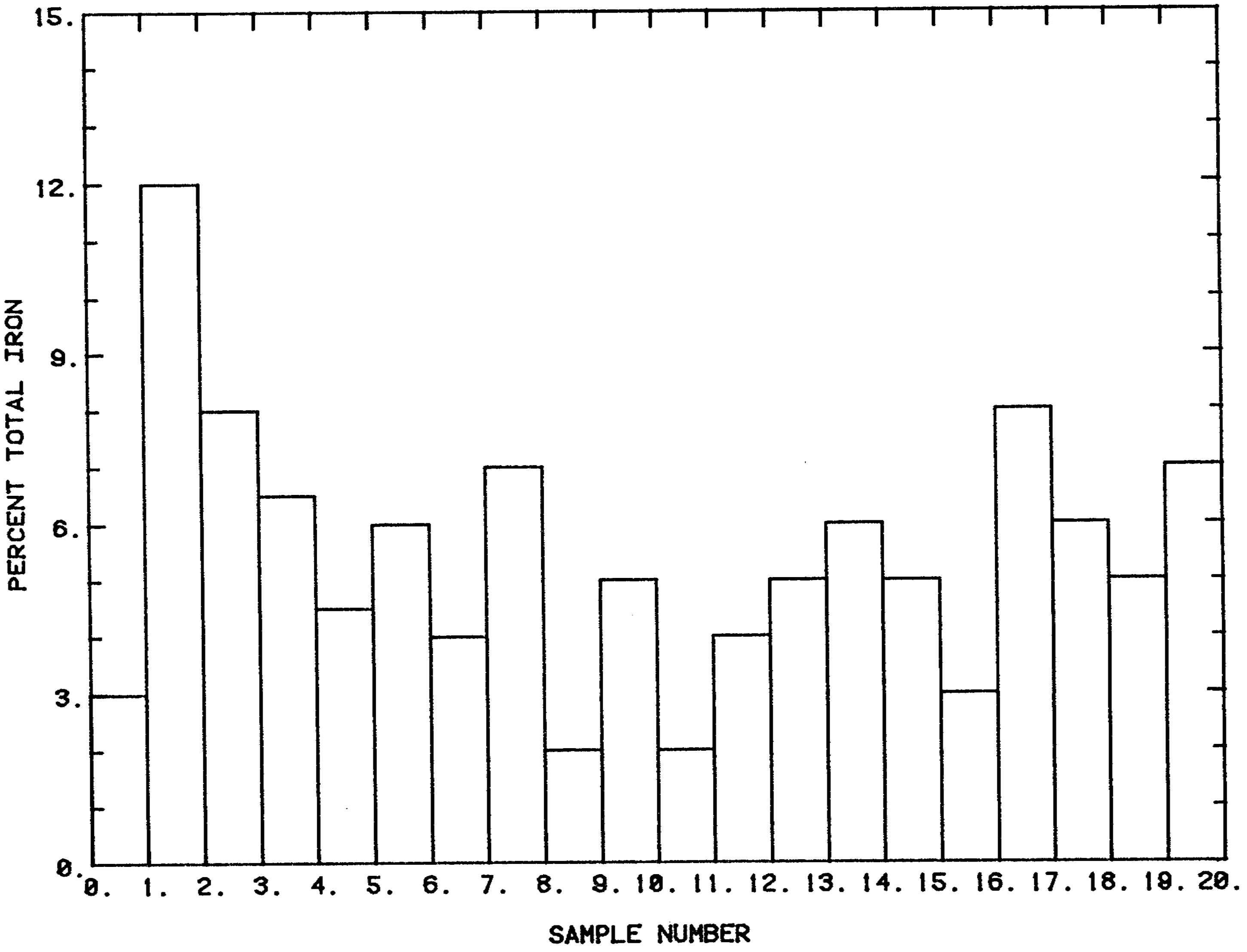

Figure 7. Percent total iron recovered from the organic geochemical phase.

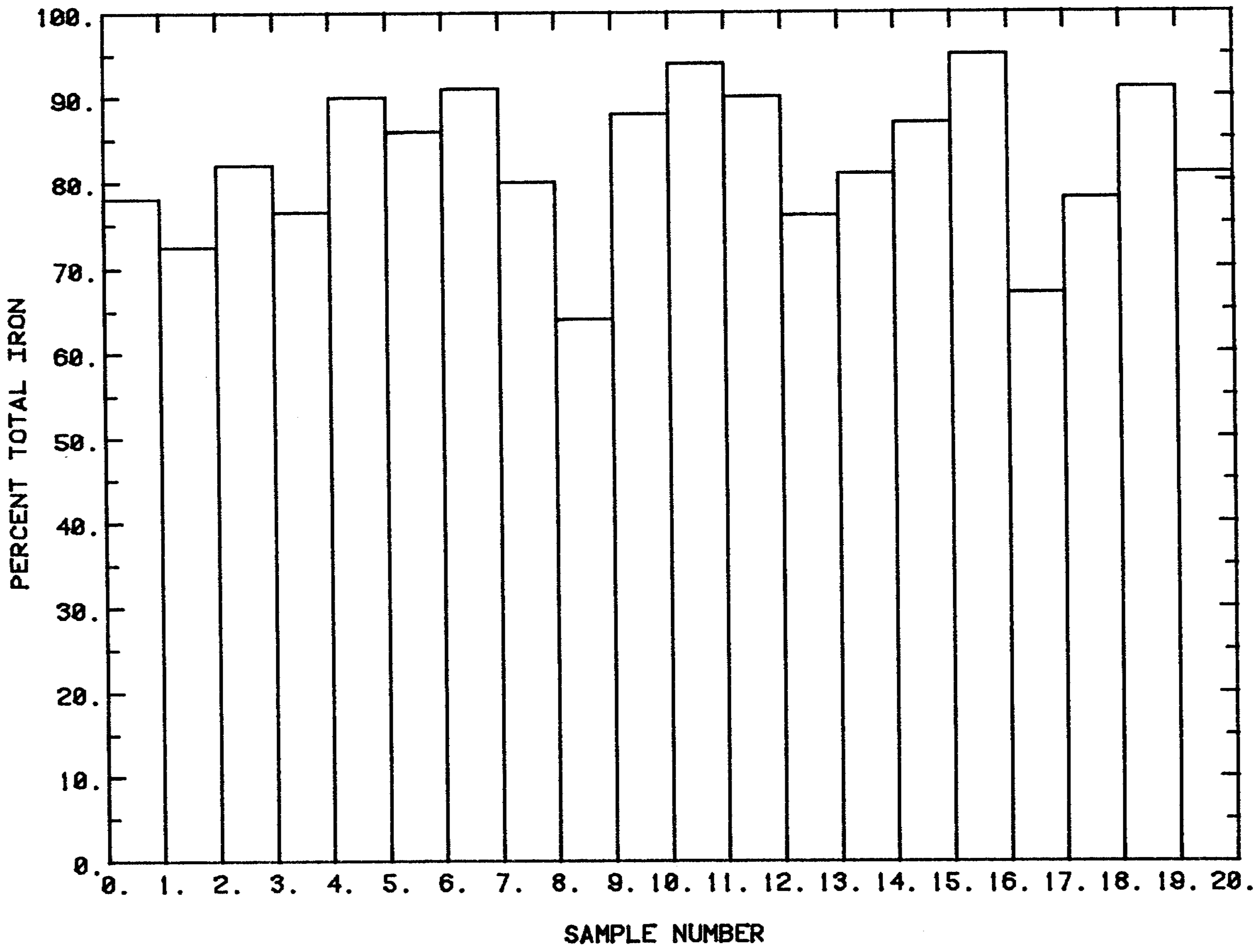

Figure 8. Percent total iron recovered from the pyrite geochemical phase.

(p.245, 1976) for 10 Raton coals. Pillmore does not include a discussion of possible mineral species present in the coals. The difference in pyrite content may (1) reflect a variance within York Canyon coal or (2) suggest that iron identified as pyritic iron is being recovered from some other geochemical phase. If statement (2) were true, a possible candidate would be the clay fraction within the coal. The pyritic iron content of NBS Standard Reference Material 1635 was determined using the standard ASTM method. Extraction was done in triplicate. The concentration of pyritic iron determined by this method was 1798 ppm. This value is 22 percent greater than the lower value of 1479 ppm and 15 percent less than the larger value of 2118 ppm determined for this coal during the sequential extraction process. This fact appears to help substantiate the pyritic iron values. X-ray examination of material remaining after the oxidation of hydrocarbon material was not done due to the small amount of material remaining after oxidation.

Total iron content in parts per million is shown in Figure 9 (see Table 1 for sample identification) and listed in Appendix 6A. This figure shows Mulford, western Kentucky coal (16815-2), to have the highest iron content (13,551 parts per million) and New Mexican Navajo coal, sample 16727-5, the lowest (1294 parts per million). The mean iron content for the Raton samples (samples 16727-6, C 86 D, C 87 D, and C 88 D) is 0.53% (whole-coal weight percent) which compares to reported iron values for this coal. Pillmore (1976) cites an expected iron value of 0.49% for York Canyon, Raton Coal but reports a range of 0.34-0.81% (whole-coal basis). This cited range appears to be different than the amount of pyrite iron calculated from the forms

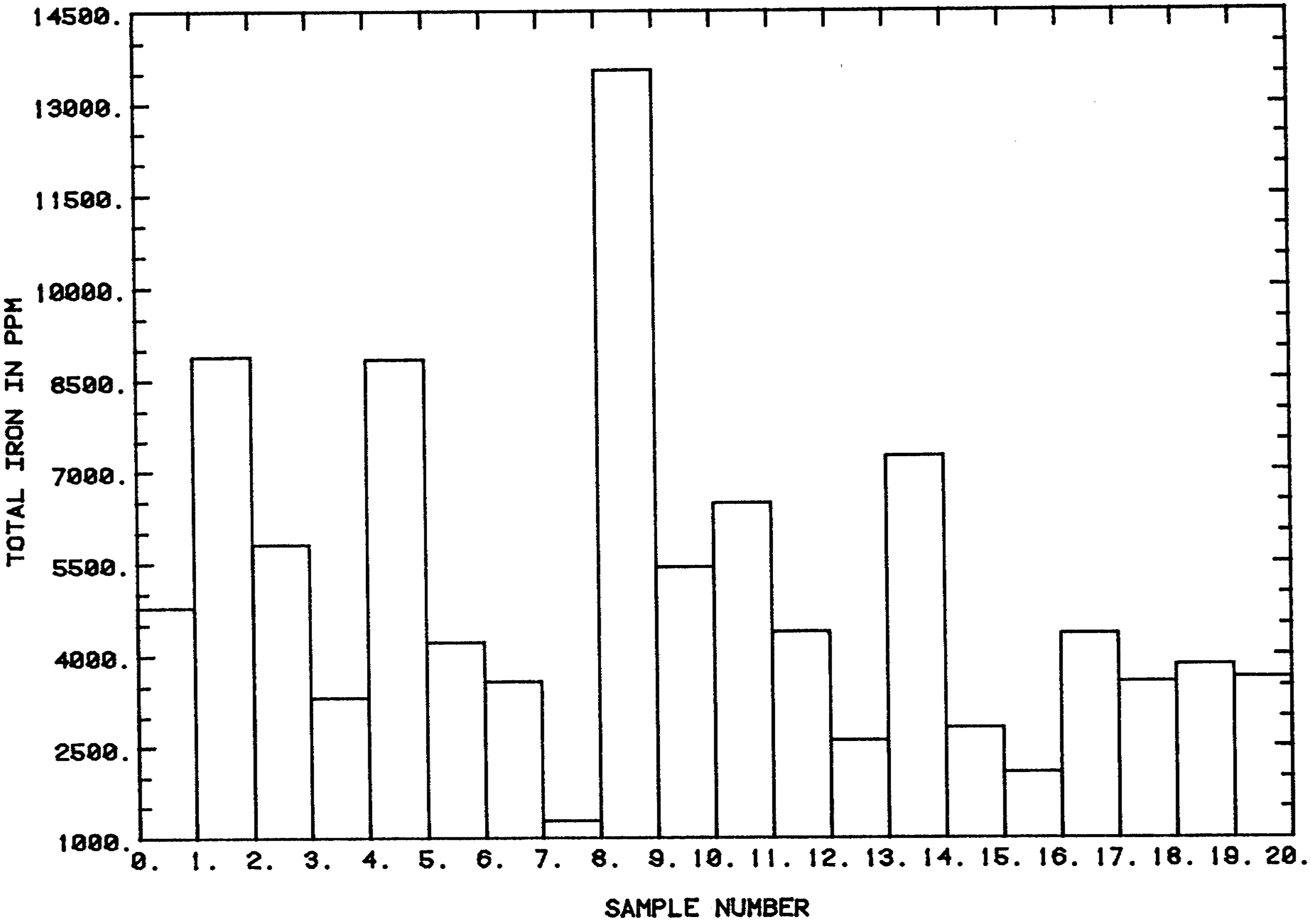

Figure 9. Total iron recovered in parts per million (ppm).

of sulfur data mentioned previously.

The iron concentration of each geochemical fraction within its phase was calculated. Organic iron occurs within the hydrocarbon phase. This phase includes the volatile matter and the fixed carbon content. Organic iron concentration within its phase is equal to the weight percent of organic iron divided by the sum of the weight percents of the volatile matter and fixed carbon. Exchangeable iron, carbonate iron and oxide iron occur within the non-pyrite inorganic fraction of the coal. Concentration of iron within this fraction was calculated by dividing the appropriate weight percent iron by weight percent mineral matter minus weight percent pyrite. These calculated concentrations, total iron content, percent pyrite, and calculated distribution coefficients were plotted against percent mineral matter and percent fixed carbon (dmmf) using SPSS (Statistical Package for the Social Sciences, Nie et al., 1975). The SPSS program prepares correlation plots of selected data, evaluates degree of linear correlation, computes correlation coefficient (R), variance (R squared), significance, and error estimate for a line of slope (b) and y intercept (a). R and R2 values measure the strength of linear relationship. SPSS plots and statistical summaries are in Appendix 10. Selected plots are reproduced in figures 10 to 21.

A mild positive dependence (R = 0.56247; R2 =0.31637; significance = 0.00350) occurs between pyrite and percent mineral matter (Appendix 10). This correlation improves when western Kentucky Mulford coal is excluded. This coal has high iron and sulfur contents but is low in ash (6.56%) making its concentration anomalously high compared to the other coals. If New Mexican coals are considered as a group, the positive correlation becomes more significant (R = 0.80; R2 = 0.64; significance = 0.00003). This same trend is apparent when considering total iron (Appendix 11). The weak positive relationship (R = 0.43196; R2 = 0.18659; significance = 0.02859) strengthens (R = 0.81288; R2 = 0.66077; significance = 0.00004) when the New Mexican coals are grouped.

Figure 10 shows a mild correlation between the concentration of organic iron within its phase and mineral matter (R = 0.68387; R2 = 0.46768; significance = 0.00044). This relationship does not change significantly when New Mexican coals are grouped.

No relationship (Figure 11) seems to exist between percent mineral matter and the concentration of oxide iron within the non-pyrite inorganic coal fraction.

Figure 12 shows a strong negative correlation (R = -0.91826; R2 = 0.84321) between the concentration of carbonate iron within its phase and percent mineral matter. However, due to the small number of points, the correlation may not be statistically significant.

The correlation plot (Figure 13) for exchangeable iron within the non-pyrite inorganic phase is included for completeness. No trend is shown. The exchangeable iron concentration of western Kentucky Mulford coal is about one hundred times greater than New Mexican coals.

The relationship between total iron and mineral matter is not unexpected due to the availability of iron. The mild correlation of pyritic iron and lack of correlation of oxide iron

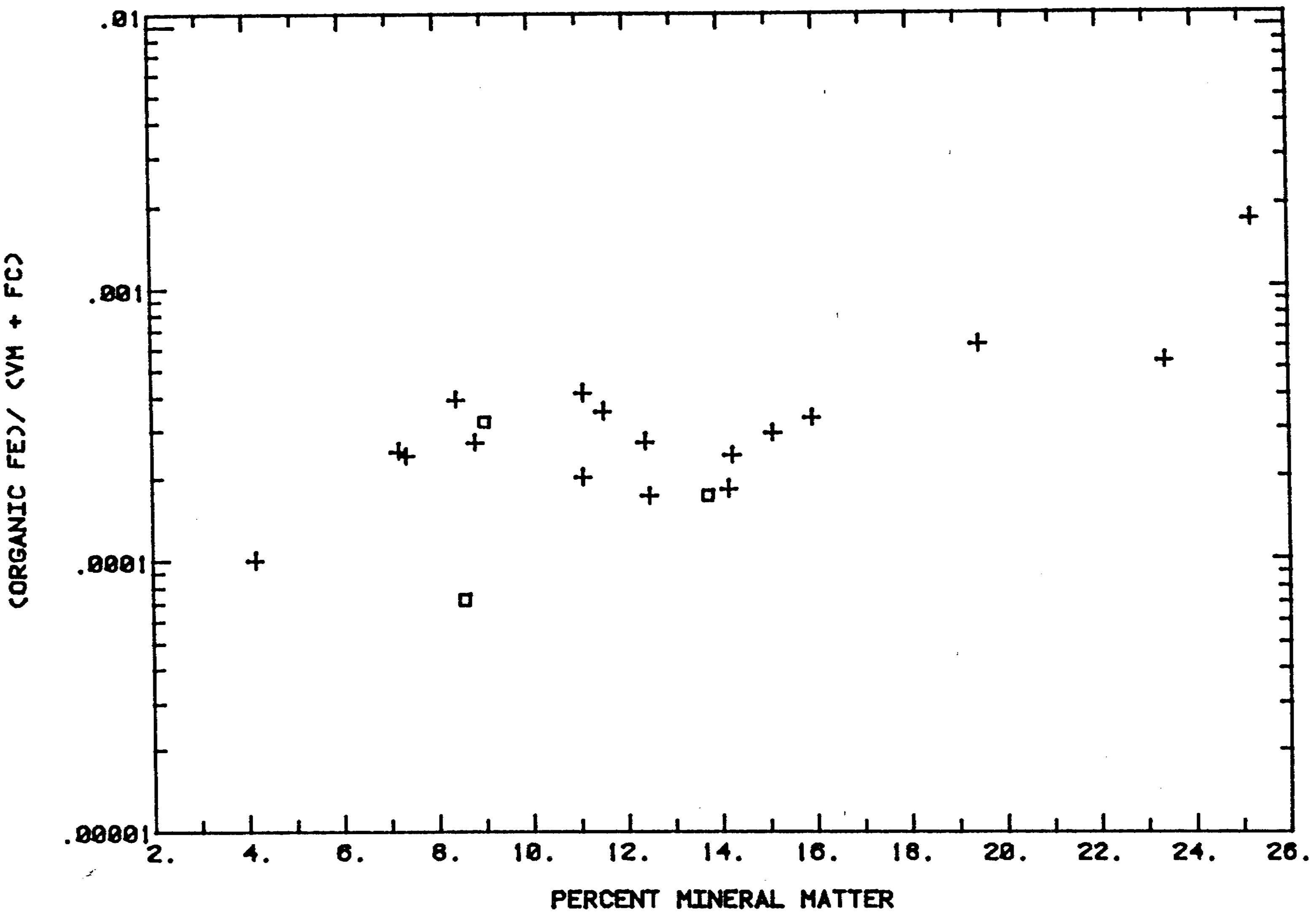

Figure 10. Concentration of organic iron within the hydrocarbon fraction of the coal compared to percent mineral matter. + = western coal, □ = eastern coal

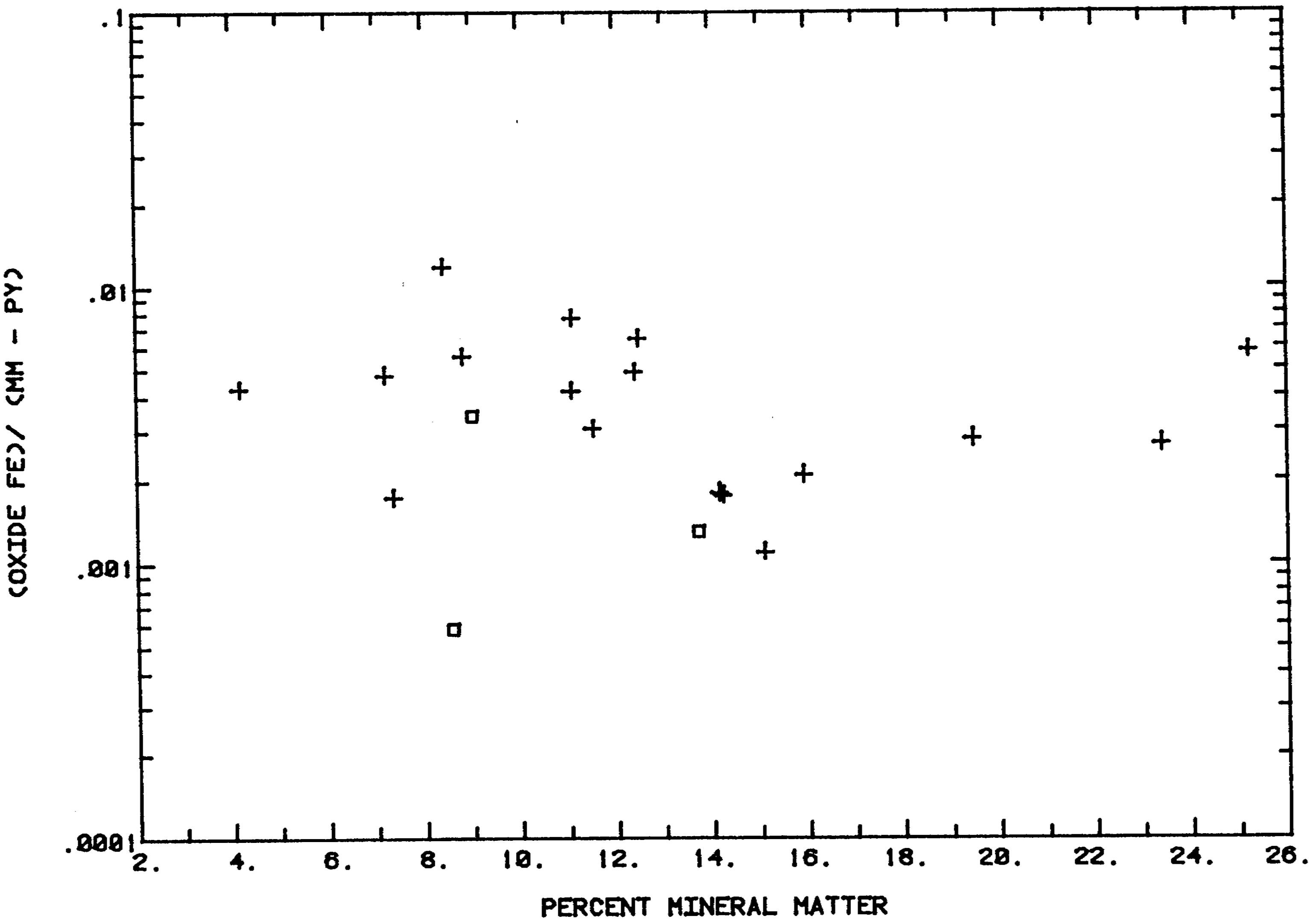

Figure 11. Concentration of oxide iron within the non-pyritic inorganic coal fraction compared to mineral matter.
+ = western coal ▫ = eastern coal

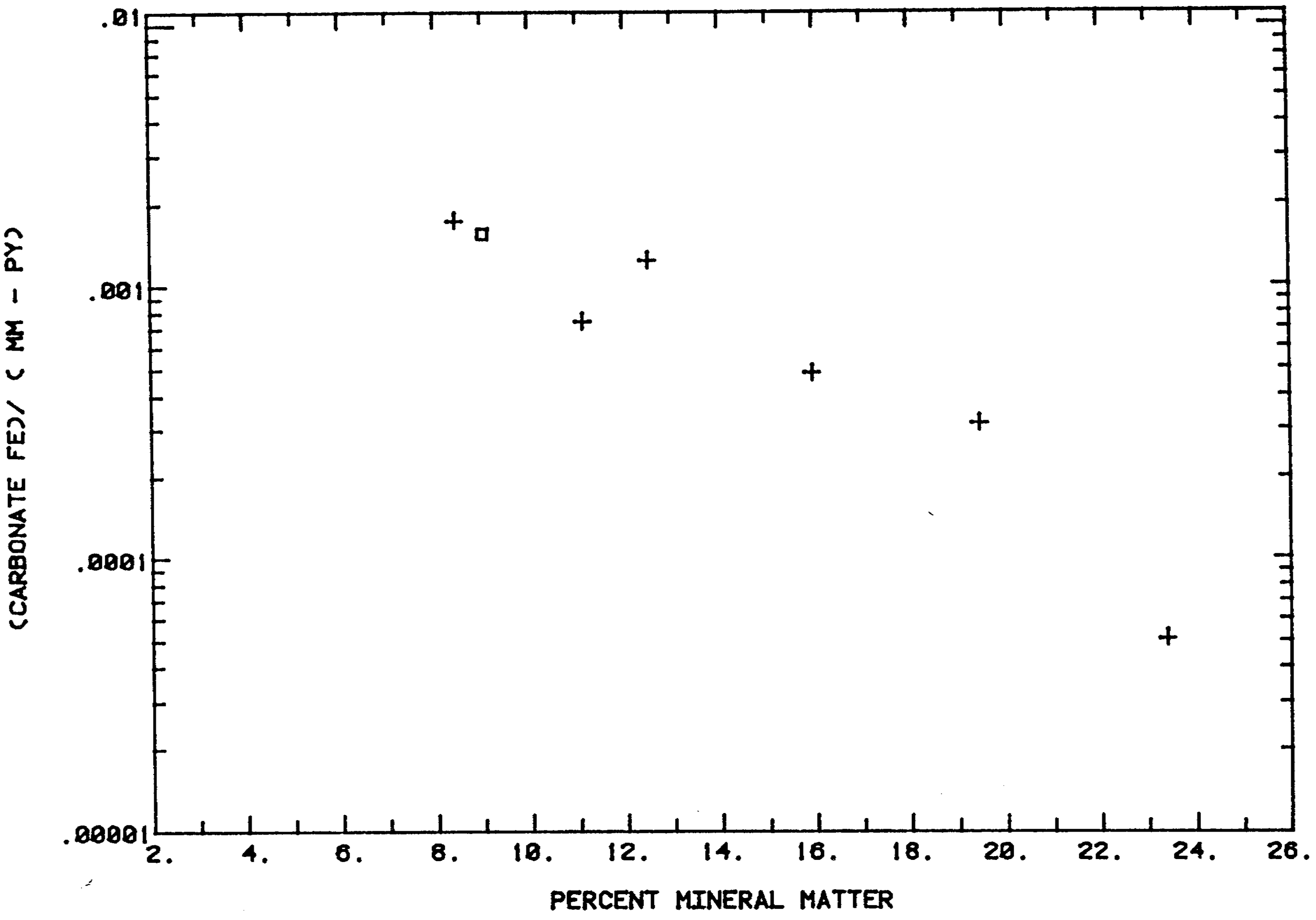

Figure 12. Concentration of carbonate iron within the non-pyritic inorganic coal fraction compared to mineral matter.
+ = western coal ◻ = eastern coal

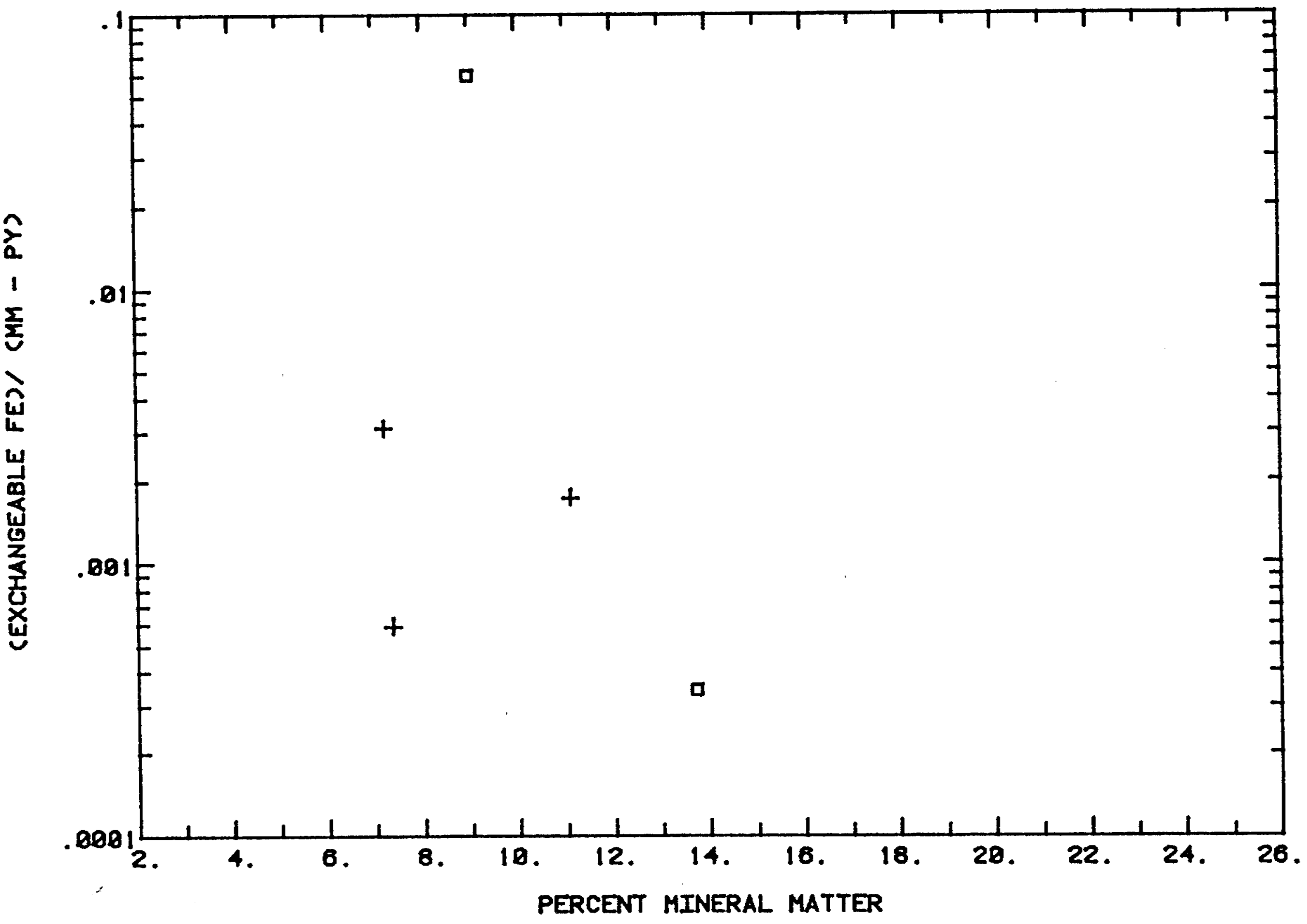

Figure 13. Concentration of exchangeable iron within the non-pyritic inorganic coal fraction compared to percent mineral matter. + = western coal; ◻ = eastern coal;

concentration to percent mineral matter potentially supports the scavenging ability of iron and its preference for sulfur during coalification. Although the statistical sampling is sparse, the correlation between organic iron and percent mineral matter may suggest that the presence of increased amounts of mineral matter heightens the possibility of either 1) inclusion of minute syngenetic particles within the hydrocarbon material which are impossible to isolate but are easily solubilized due to size or 2) additional metallic-organic molecule formation. An increase in such molecular formation could indicate specific Eh/pH conditions or a decreased organic/metallic ratio conducive to such molecular formation.

The distribution coefficient, (K), describes the distribution of iron between the non-pyritic inorganic and hydrocarbon fractions of coal. This coefficient was calculated as follows:

$$K = \frac{[Fe1]}{[Fe2]}$$

where the concentration of iron within the non-pyritic inorganic phase, Fe1 is:

$$Fe1 = \frac{(\text{non-pyritic inorganic iron})}{(\text{mineral matter - pyrite})}$$

and the iron concentration within the organic hydrocarbon phase, Fe2 is:

$$Fe2 = \frac{(\text{organic Fe})}{(\text{fixed carbon + volatile matter})}$$

pyrite = weight percent pyritic iron x 1.875

The value 1.875 is a gravimetric factor equal to the gravimetric weight of pyrite (120), divided by the gravimetric weight of iron (56). Fe1 was considered to be equal to the concentration of oxide iron within the non-pyrite inorganic mineral matter.

In order to calculate the distribution coefficient, the as-received proximate analyses were normalized to mineral matter content by the following relationship: moisture + mineral matter + volatile matter + fixed carbon = 100%. These values are listed is Appendix 2B. Specific values used in calculating distribution coefficients are listed in Appendix 7.

Figure 14 shows a slight negative relationship between distribution coefficient values, defined above as K, and percent mineral matter content (R = -0.58075; R2 = 0.33728; significance = 0.00303). This relationship reflects the correlations already mentioned i.e. the changes in concentration of oxide iron and organic iron within their respective phases with percent mineral matter. The negative trend reflects the increase in organic iron with increased mineral matter.

Figures 15 through 19 show that, with the possible exception of the oxide iron concentration (Fig. 17), which shows a mild positive relationship (R = 0.47928; R2 = 0.22972; Significance = 0.01625), no relationship is recognized between fixed (dmmf) carbon content and the iron concentration of any geochemical phase or distribution coefficient.

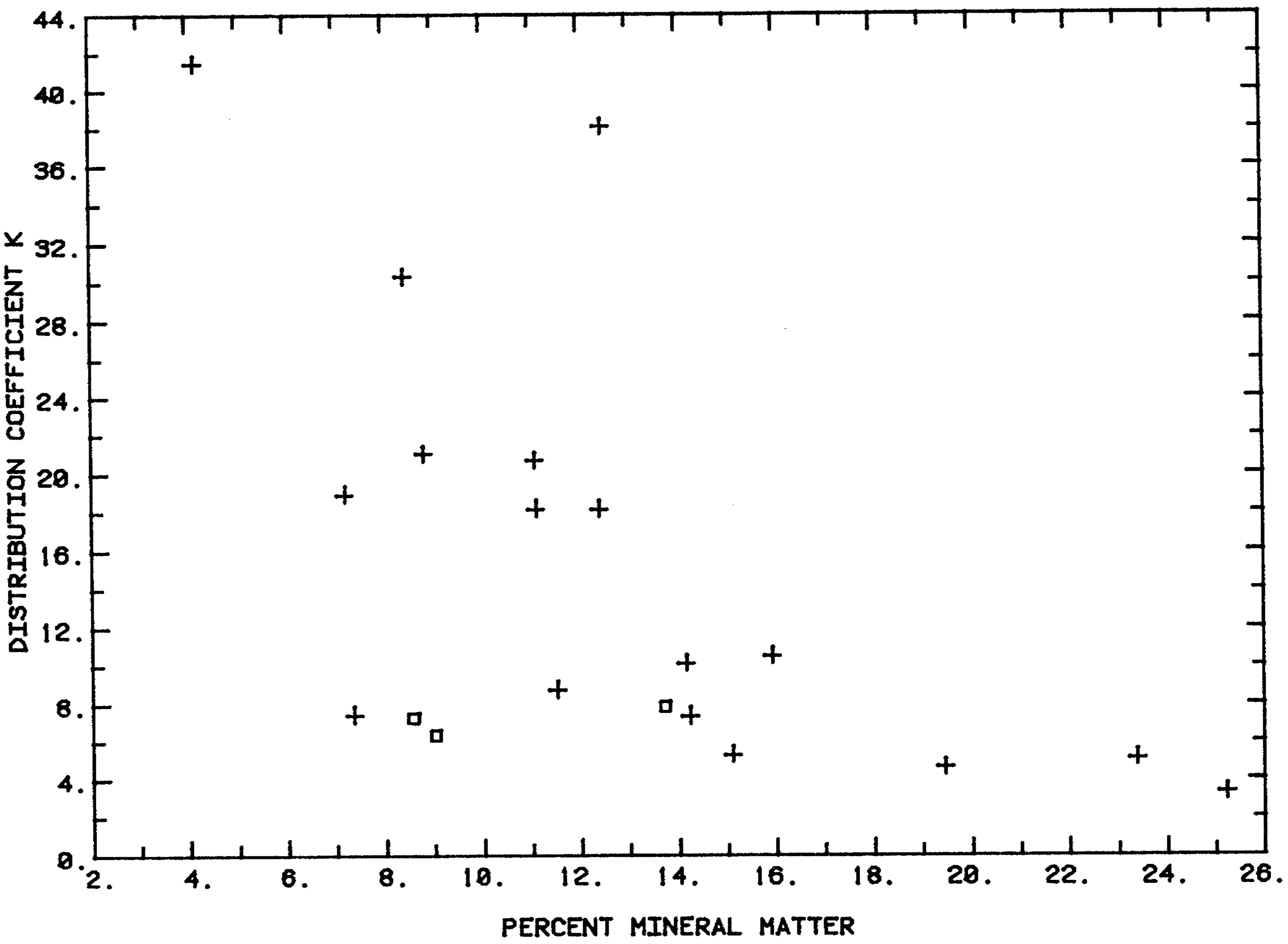

Figure 14. Distribution coefficient, K, compared to percent mineral matter.
+ = western coal ▫ = eastern coal

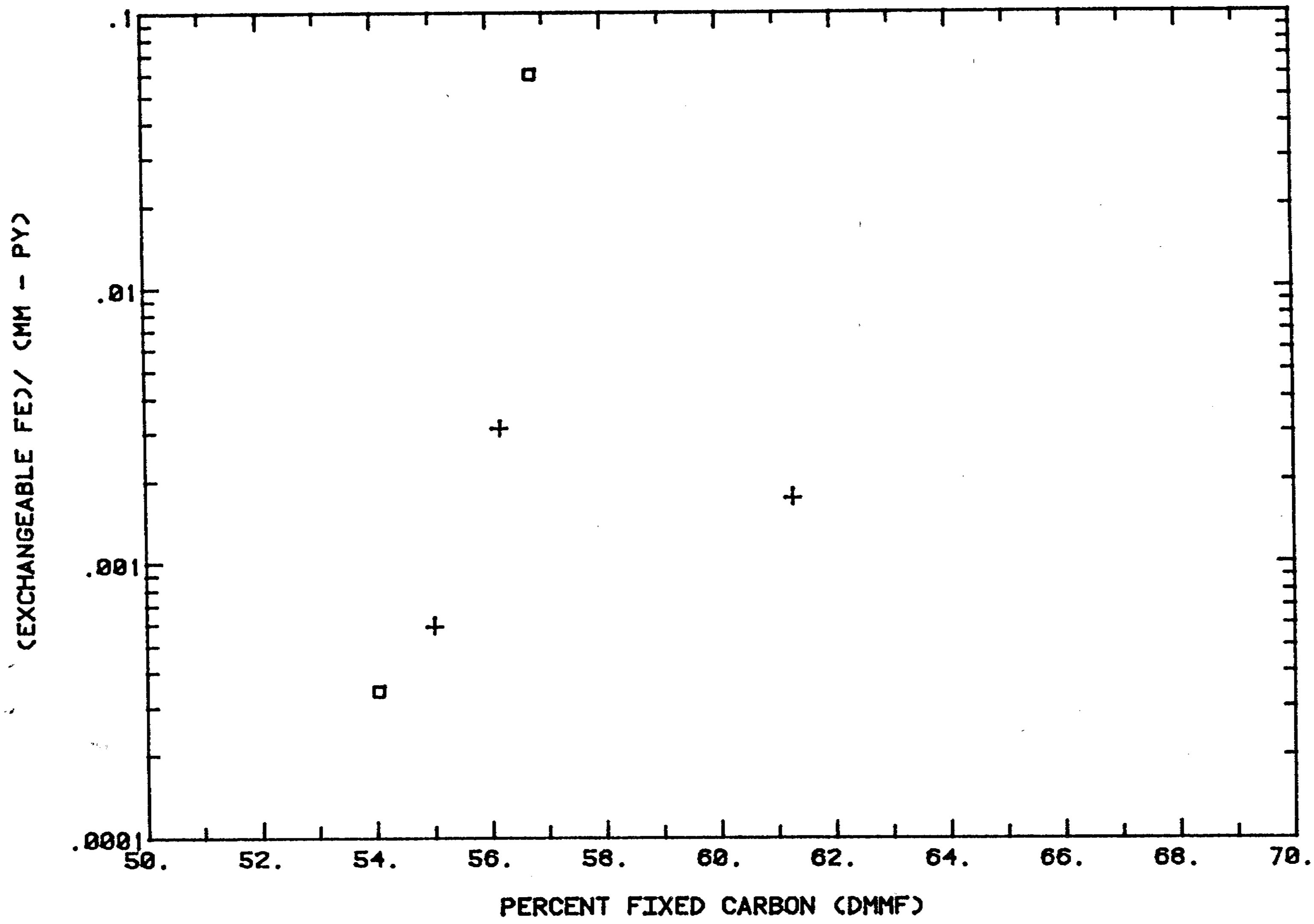

Figure 15. Concentration of exchangeable iron within the non-pyritic coal fraction compared to percent fixed carbon (dmmf).
+ = western coal □ = eastern coal

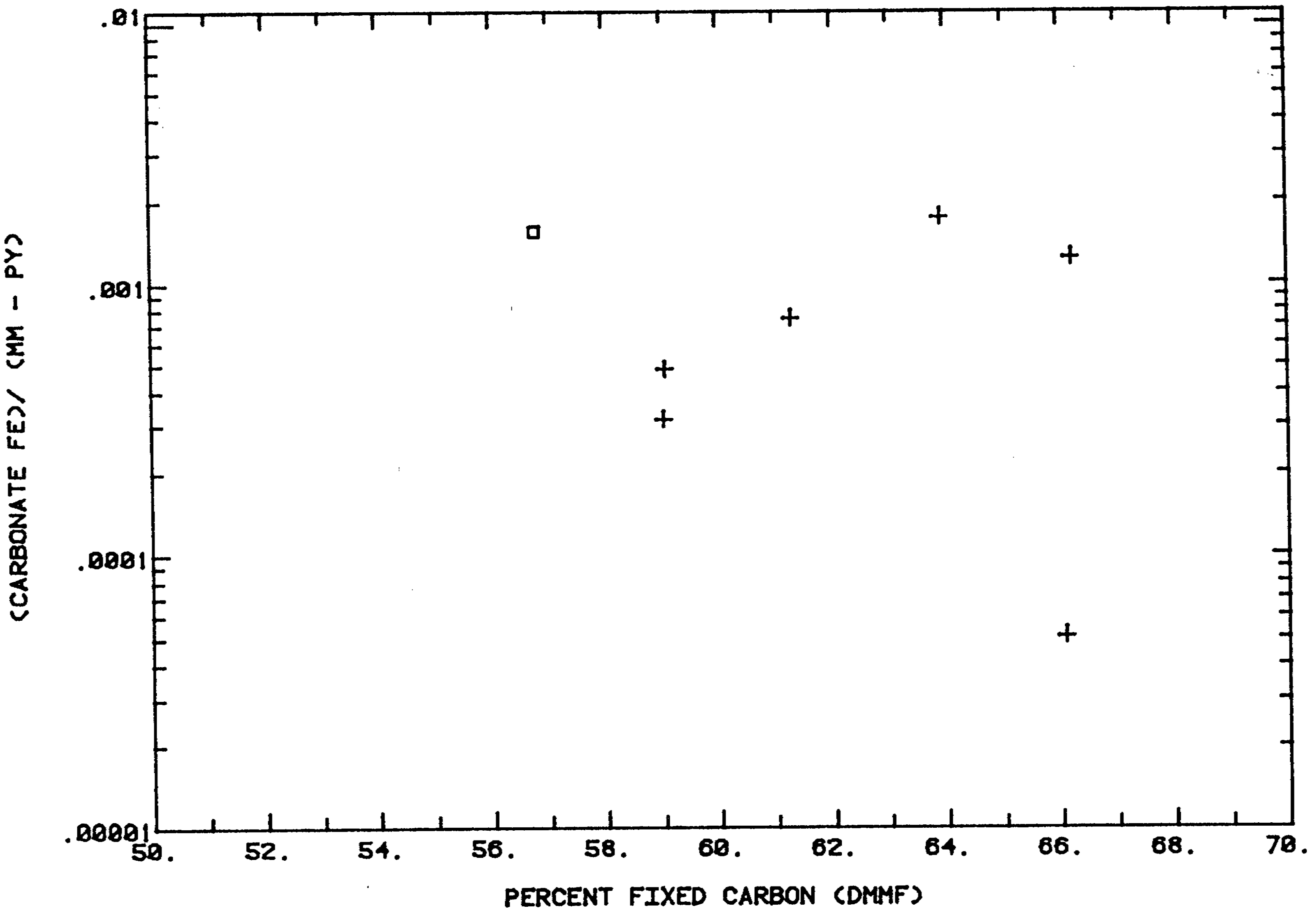

Figure 16. Concentration of carbonate iron within the non-pyritic coal fraction compared to percent fixed carbon (dmmf)

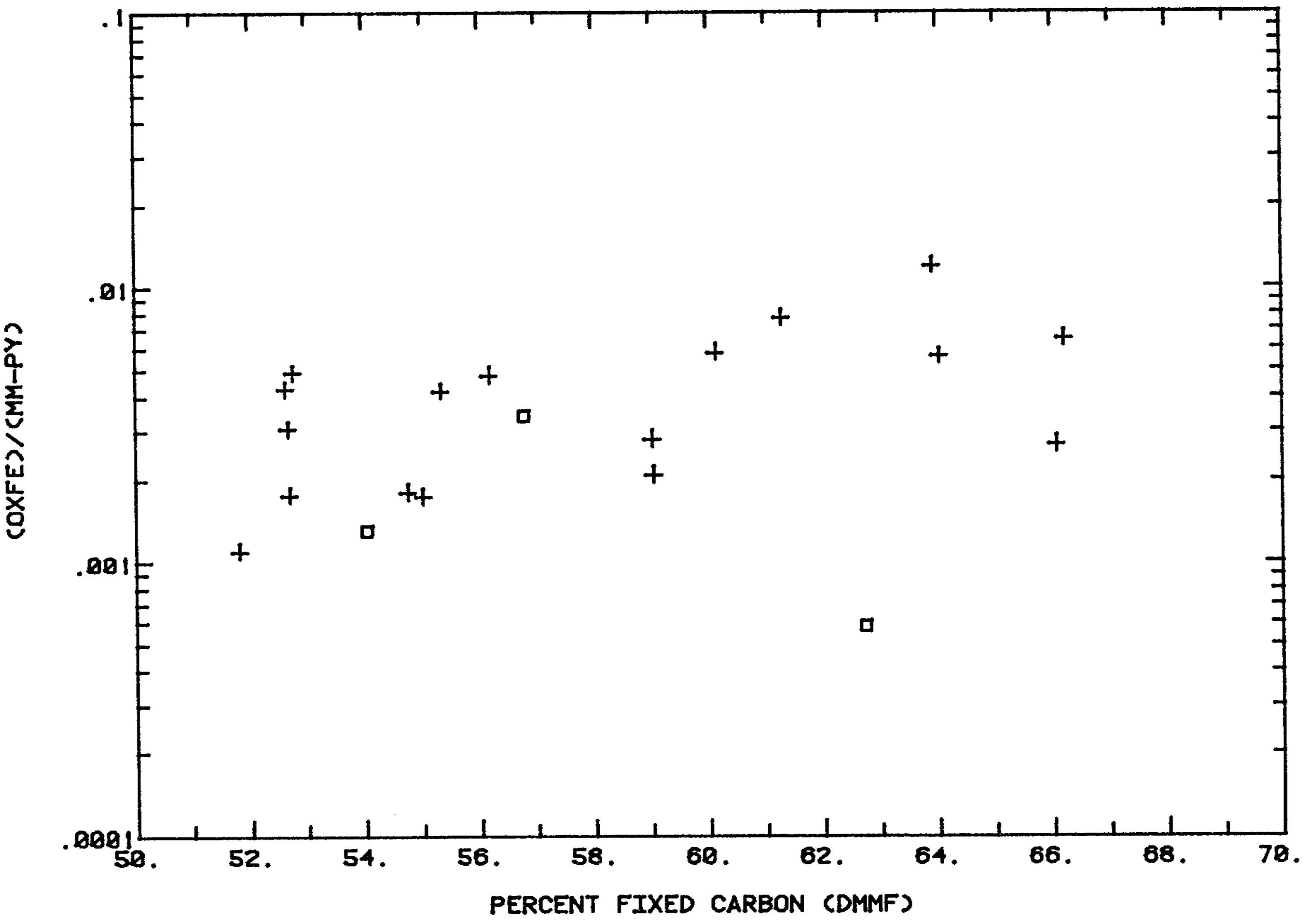

Figure 17. Concentration of oxide iron within the non-pyritic coal fraction compared to percent fixed carbon (dmmf).

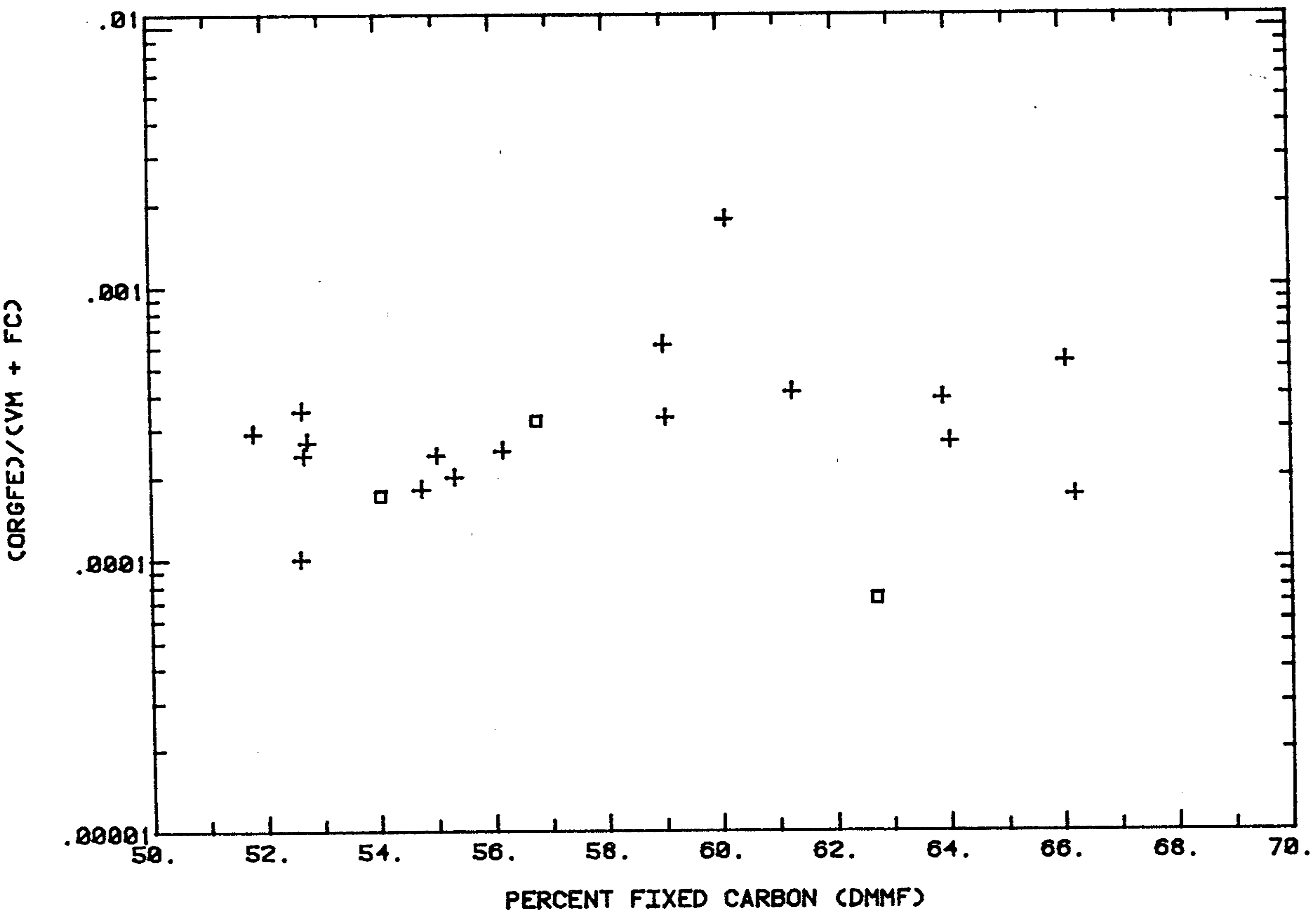

Figure 18. Concentration of organic iron within the hydrocarbon coal fraction compared to percent fixed carbon (dmmf)

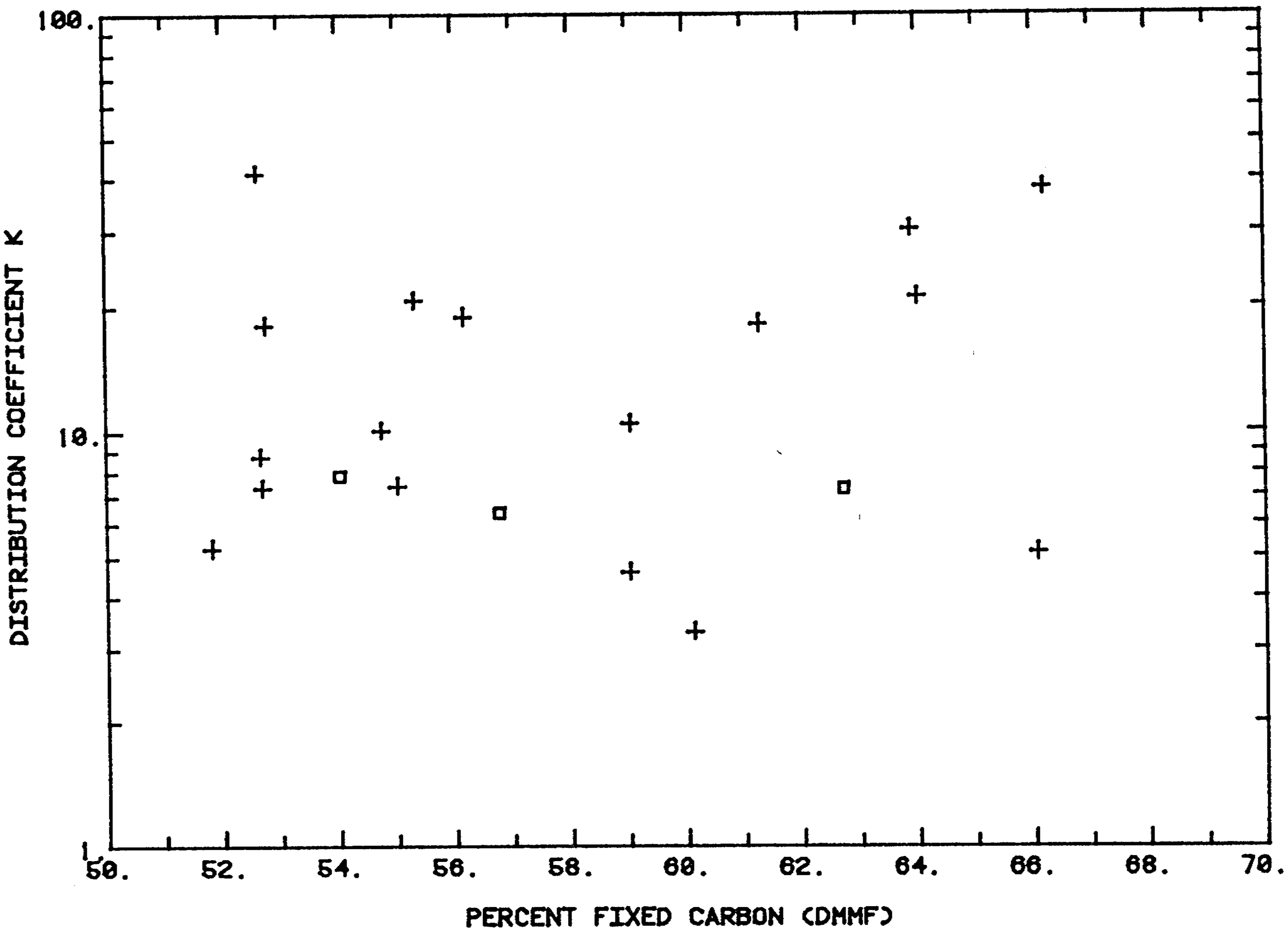

Figure 19. Distribution coefficient, K, compared to percent fixed carbon (dmmf).
+ = western coal ◻ = eastern coal

Appendix 2A lists moisture and mineral matter free heating values (BTU/lb). Using these values, the coals used in this study range in rank from subbituminous C to high volatile A bituminous coal. Had coals having a wider range of fixed carbon been included in the study, a definitive relationship may have been observed between organic iron content, distribution coefficients and fixed carbon (dmmf) values. As previously mentioned, some researchers support the idea of the potential for higher levels of metallo-organic complex formation in low rank coals. The higher level is thought to reflect a larger number of available metallic-organic bonding sites and greater permeability in lower rank coals. The number of bonding sites and permeability are thought to decrease as the rank increases. The decrease in bonding sites with its accompanying decrease in metallo-organically bound iron would be reflected as a decrease in the concentration of organic iron within its phase. A decrease in this value would cause the distribution coefficient K to increase with rank if there were no corresponding decrease in the non-pyritic iron concentration. The fact that the non-pyritic inorganic iron concentration value was the only value to show any measurable relationship to the fixed carbon content (dmmf) supports the hypothesis that the distribution coefficient should increase with rank, i.e., show a positive trend.

Distribution coefficients were calculated from sample data published by the Illinois State Geological Survey (Gluskoter, H.J., Ruch, R.R., Miller, W.G., Cahill, R.A., Dreher, G.G., and Kuhn, J.K., 1977). This was done to evaluate correlative results based on distribution coefficients calculated from iron values obtained by methods different than those used in the present study. Tables 2 through 5 list the pertinent data. These tables were taken directly from: Trace Elements in Coal: Occurrence and Distribution (Gluskoter et al, 1980). Only data for the selected samples are reproduced. Values used for calculating the distribution coefficients are given in Appendix 8, parts A,B, and C. As previously noted distribution coefficient, K, is considered to be equal to the concentration of non-pyrite inorganic iron within its phase (mineral matter-pyrite content) divided by the concentration of organic iron with its phase (hydrocarbon). The forms of sulfur data were used to calculate weight percent pyritic iron. This pyritic iron value was found to be larger than the total iron for five samples (C18560, C18841, C18857, C14684, and C15999 - all are from Illinois) In order to calculate the distribution coefficients for these five samples, an average of the total iron values for the other samples was found. This value was used to calculate non-pyritic inorganic iron values. Organic iron equals the iron content of the demineralized coal. Non-pyritic inorganic iron is equal to the total iron content minus organic and pyritic iron contents.

Figures 20 and 21 show the distribution coefficients of the selected samples plotted against percent mineral matter and percent fixed carbon (dmmf). There appears to be a very mild positive relationship (R = 0.41880; R2 = 0.17539) between the distribution and mineral matter. The observed relationship reflects that either: (1) free iron was not completely taken up by "sulfide ion" to form pyrite; (2) organic iron content decreased; or (3) a combination of one and two. The mild trends exhibited by these data and that of the present study make drawing a conclusion

Table 2: Whole Coal Identification of Gluskoter Selections

Sample	Coal Seam	State
C16543	Herrin (No. 6)	Illinois
C17001*	Davis	Illinois
C18304	De Koven	Illinois
C18560*	Herrin (No. 6)	Illinois
C18816	Mammoth	Montana
C18820*	Pocahontas (No. 4)	West Virginia
C18841*#	Pittsburgh (No. 8)	West Virginia
C18848*#	Blue Creek	Alabama
C18857	Herrin (No. 6)	Illinois
C19000*#	Black Mesa Field	Arizona
C18844	Pittsburgh (No. 8)	Pennsylvania
C18824	Johnson	Alabama
C18440#	Noonan	North Dakota
C18320	Herrin (No. 6)	Illinois
C18368	Herrin (No. 6)	Illinois
C18445	Rosebud	Montana
C18457	Hanna 24	Wyoming
C14684	Herrin (No. 6)	Illinois
C15999	Herrin (No. 6)	Illinois

*Samples for which gravity separations were made.

#Samples for which ion exchange determinations were made.

(Source: Kuhn, Jlk., Kiene, F.L., Cahill, R.A., Gluskoter, H.J., Shimp, N.F., Aug. 1980, page 5)

Table 3: Proximate Analyses of Whole Coal Samples (percent whole coal except for Btu values)

Sample Number	Adl	Mois	V.M.	F.C. (dmmf)	Ash	Btu	F.C.
C16543	9.40	17.00	43.00	45.10	11.90	12380	51.20
C17001	4.10	5.90	39.50	48.70	11.80	12947	55.21
C18304	---	2.40	40.50	48.60	10.90	13182	54.55
C18560	7.20	9.10	41.60	42.00	16.50	11714	50.31
C18816	---	13.20	38.70	52.30	9.00	12095	57.47
C18820	0.70	1.90	16.60	71.90	11.50	13763	81.24
C18841	0.50	2.30	42.50	47.30	10.20	13155	52.67
C18848	0.60	1.90	20.00	68.40	11.70	13628	77.46
C18857	11.90	14.40	39.80	46.30	13.90	12082	53.78
C19000	4.60	8.90	43.00	50.00	7.00	12475	53.77
C18844	0.80	2.40	35.70	56.00	8.30	13816	61.07
C18824	1.80	3.20	24.70	62.80	12.50	13528	71.77
C18440	12.60	19.40	39.70	50.50	9.80	10967	56.02
C18320	7.80	9.80	38.70	47.60	13.80	12094	55.23
C18368	7.00	11.00	39.80	47.00	13.20	12198	54.15
C18445	17.10	22.90	41.40	51.10	7.50	11733	55.24
C18457	10.40	18.60	48.90	44.80	6.30	11688	47.82
C14684	6.00	8.50	38.20	51.80	10.00	12934	57.55
C15999	4.10	7.30	38.00	49.60	12.40	12470	56.62

(Source: Kuhn, J.K., Fiene, F.L., Cahill, R.A., Gluskoter, H.J., Shimp, N.F., Aug. 1980, page 34)

Table 4- Sulfur Analyses of Whole Coal Samples
(percent, moisture-free whole coal basis)

Sample	ORS	PYS	SUS	TOS	SXRF
C16543	1.91	1.21	0.04	3.15	3.32
C17001	1.51	2.62	0.02	4.14	3.49
C18304	1.55	2.63	0.07	4.25	3.15
C18560	1.87	4.56	0.02	6.45	6.52
C18816	0.45	0.54	0.01	1.00	0.85
C18820	0.51	0.26	0.03	0.80	0.95
C18841	2.51	2.48	0.03	5.02	4.81
C18848	0.50	0.04	0.01	0.55	0.74
C18857	2.42	2.51	0.09	5.02	4.85
C19000	0.52	0.08	----	0.61	0.76
C18844	1.16	1.14	0.03	2.33	2.16
C18824	0.54	0.43	0.01	0.98	1.07
C18440	0.47	0.01	0.03	0.51	0.54
C18320	1.83	1.83	0.05	3.71	3.43
C18368	2.08	1.84	0.02	3.94	3.86
C18445	0.60	0.23	0.02	0.84	0.76
C18457	0.25	0.17	0.07	0.50	0.49
C14684	1.33	1.44	0.02	2.79	2.46
C15999	1.44	1.79	0.08	3.31	3.04

(Source: Gluskoter, Ruch, Miller, Cahill, Dreher, and Kuhn, 1977, page 38)

Table 5: Comparison of Trace and Minor Elements in Raw and Demineralized Coal

Iron			
Sample Number	Raw Coal (percent)	MMF* (ppm)	Retention# (percent)
C16543	1.59	93	0.6
C17001	2.76	64	0.2
C18304	2.79	100	0.4
C18560	2.60	66	0.3
C18816	0.60	60	1.0
C18820	0.56	72	1.3
C18841	1.73	242	1.4
C18848	0.70	54	0.8
C18857	2.20	67	0.3
C19000	0.40	225	5.6
C18844	1.30	146	1.1
C18824	0.61	46	0.8
C18440	0.33	22	0.7
C18320	1.81	55	0.3
C18368	2.10	50	0.3
C18445	0.38	30	0.8
C18457	0.21	56	2.7
C14684	0.69	120	1.7
C15999	1.78	75	0.4

*Concentration in the demineralized residue of the 1.40 float fraction of the coal.

#Concentration in the mineral-matter-free (MMF) coal divided by the concentration in the raw coal.

(Source: Kuhn, Fiene, Cahill, Gluskoter, Shimp, Aug. 1980, page 19)

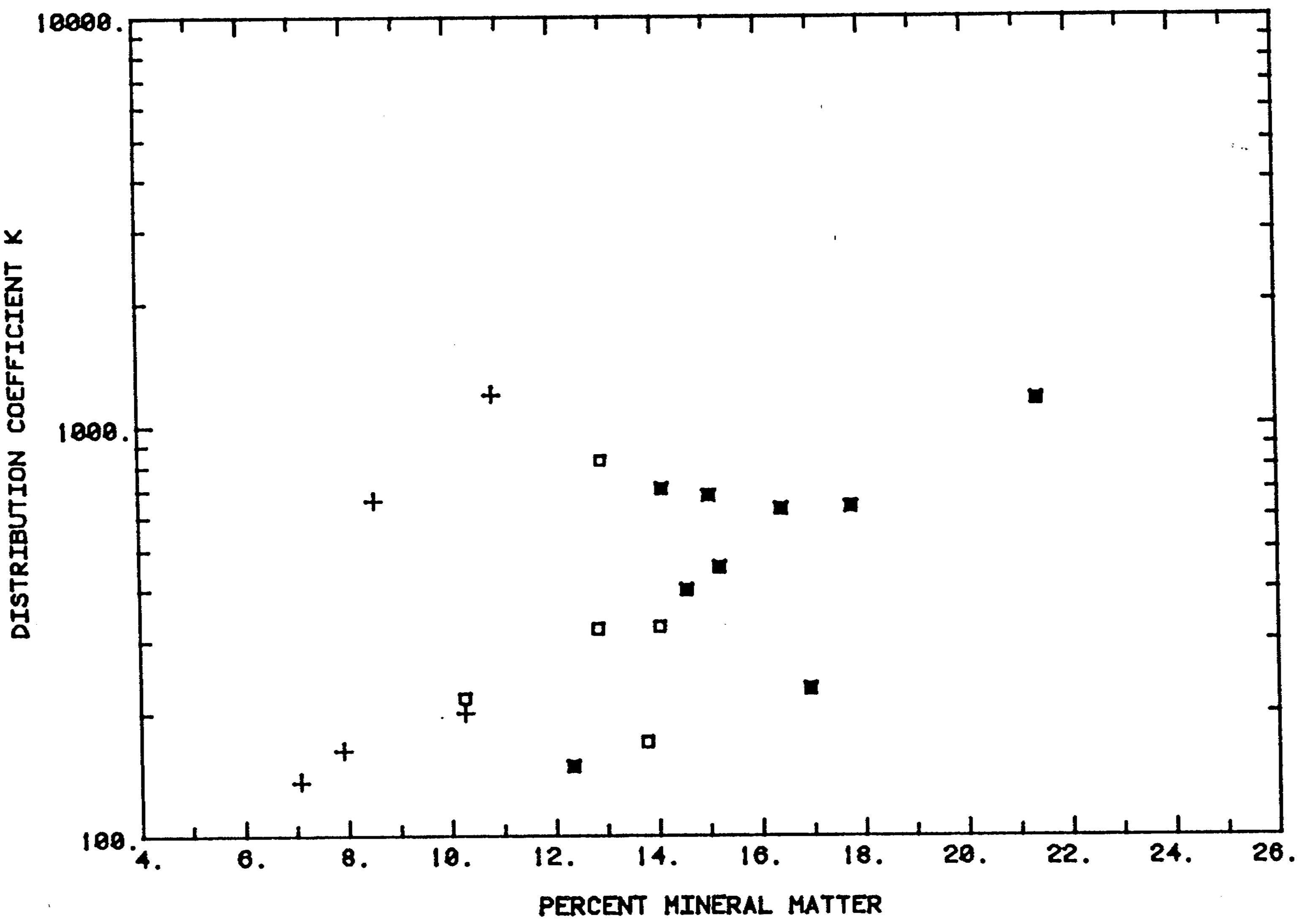

Figure 20. Distribution coefficient, K, for Gluskoter et al. data compared to percent mineral matter.
+ = western coal ◻ = eastern coal ■ = Illinois coal

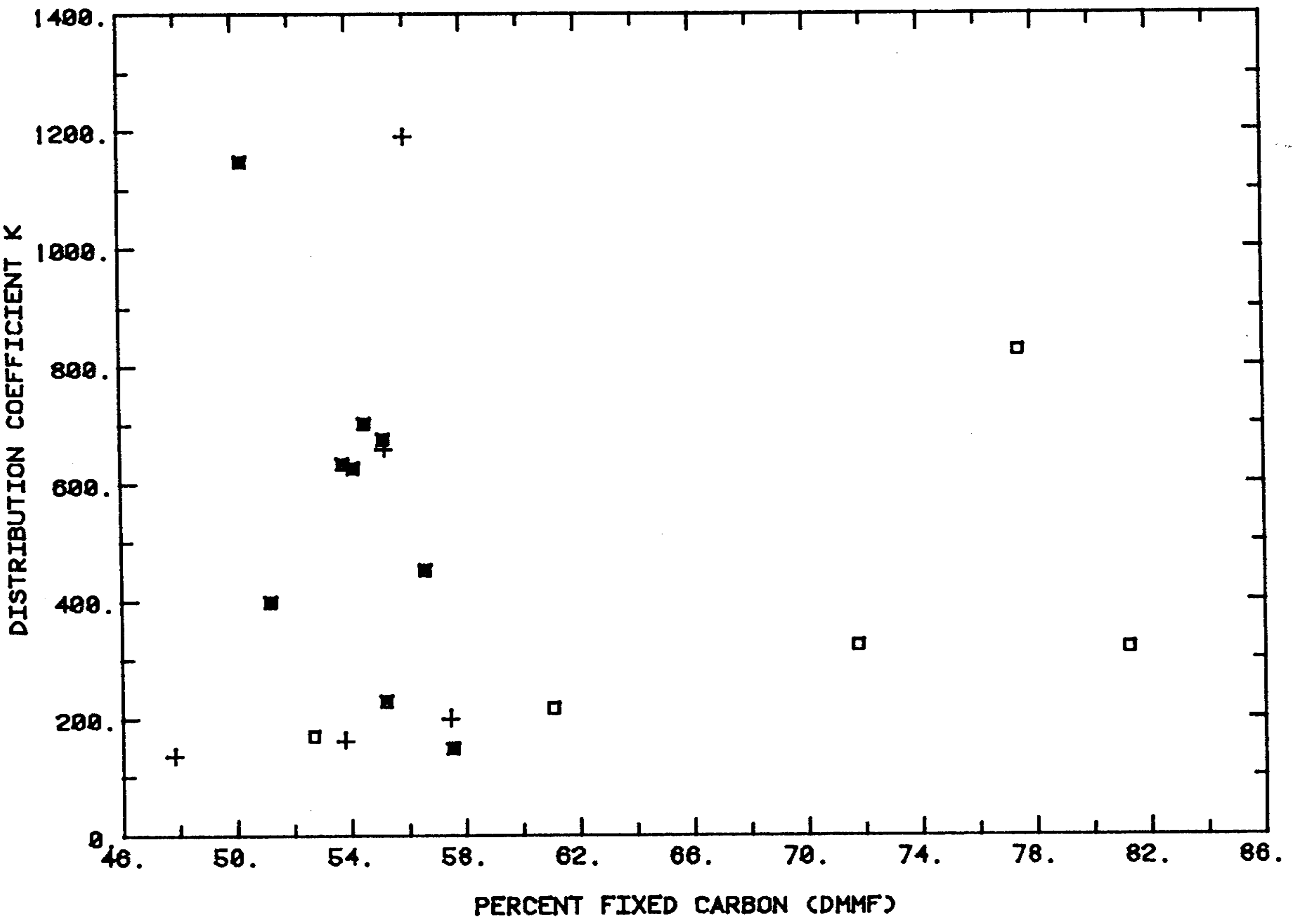

Figure 21. Distribution coefficient , K, for Gluskoter et al. data compared to percent fixed carbon (dmmf). + = western coal ◘ = eastern coal ■ = Illinois coal

inappropriate. However, based upon expectation, it would seem that demineralization may provide a better organic iron value than does the oxidation of the hydrocarbon fraction. The author suggests that organic solution of the hydrocarbon fraction with subsequent elemental determination be used for further evaluation.

No relationship was found between fixed carbon (dmmf) and the distribution coefficients for the selected Gluskoter et al. samples.

Overall iron content of the study samples is smaller than those of the selected Gluskoter samples by a factor ranging from ten to one hundred. This difference in total iron content would have influenced mineral species present in the coal.

SUMMARY AND CONCLUSIONS

Measurement of the distribution of iron among the following major geochemical phases has been accomplished: (1) exchangeable; (2) carbonate; (3) oxide; (4) organic; and (5) pyritic. Although an average of 83 percent of the total iron recovered is considered to be pyritic iron, iron was also recovered from the organic, oxide, carbonate (7 samples) and exchangeable (5 samples) geochemical phases. Weight percent pyrite was determined from the pyritic iron recovered. The concentration of iron extracted from each non-pyritic inorganic geochemical phase within the the non-pyritic inorganic mineral fraction of the coal was calculated as well as the concentration of organic iron within the hydrocarbon fraction of the coal.

These values were plotted against percent mineral matter and percent fixed (dmmf) carbon. Mild to strong relationships were noted between pyrite, total iron, the concentration of organic iron in its coal fraction, and the concentration of carbonate iron within its coal fraction and percent mineral matter. With the possible exception of oxide iron, no significant relationship was identified between the iron concentration within any coal fraction and percent fixed (dmmf) carbon.

The partitioning of an element makes possible the calculation of distribution coefficients which can be plotted against fixed (dmmf) carbon to see if the concentration of the element among the coal fractions depends upon rank. Distribution coefficients calculated from the present data were plotted against both percent mineral matter and fixed (dmmf) carbon. For comparison purposes, data published by the Illinois Geological Survey (Gluskoter et al., 1980) were used to calculate distribution coefficients which were likewise plotted against percent mineral matter and percent fixed (dmmf) carbon values.

No relationship was found between either set of distribution coefficients and percent fixed (dmmf) carbon. Therefore, it is concluded that there is no demonstratable dependency of distribution coefficients upon rank. Mild correlations occur between both sets of distribution coefficients and percent mineral matter. It is therefore concluded that there potentially is a statistical relationship between distribution coefficients and percent mineral matter and that the trend of the correlation plot can be used for interpretive purposes.

If methods can be improved for determining the elemental content of the organic fraction of coal, it would seem that distribution coefficients make possible a quantitative evaluation of the relationships between the major coal fractions. Finally, although refinement is necessary, it is suggested that the sequential extraction of coal can be used to help clarify and produce a more complete understanding of elemental distribution within coal.

SUGGESTIONS FOR FUTURE WORK

The procedure used in this study could be shortened. Partitioning between pyrite, non-pyritic inorganic and organic geochemical phases could be accomplished by using the ASTM Forms of Sulfur method for the extraction of pyritic iron and determining the iron by standard atomic absorption methods Weight percent organic iron could be determined by the high temperature ashing of a demineralized aliquot of the coal sample. Inorganic non-pyritic iron would be determinined by difference, i.e., equal total iron - (organic iron + pyritic iron). It may also be possible to determine the elemental content of coal on a whole coal basis using x-ray fluorescence. Before this could be done matrix absorption would have to be determined and infinite thickness calculated. These calculations are presently being made.

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Appendix 1

Sample Number	Location
DT519772	Mesaverde Group Upper Cretaceous
DT519771	Channel sample of unnamed coal bed, Willow Springs mine SE1/4, NW1/4, Sec. 3, T.9S., R.10E. Grab sample of unnamed coal bed.
16727-6	Raton Coal Composite
16727-2	
NM - TM	Bernalillo County, NM Crevasse Canyon Formation Upper Cretaceous Grab sample, unnamed coal bed, Tijeras Coal Field, Tocco Mine
16727-1	
419771	San Juan County, NM Fruitland Formation Upper Cretaceous Partial channel sample South Barber Pit N.E.,S.W., Sec 34,T.28N.,R.16W.
16727-5	"N"
16815-2	Western Kentucky
16815-1	
C - 7	Socorro County NM Upper Mesaverde Group Upper Cretaceous Channel sample SE, SE33, T.2N., R.4W.
16727-3	
DT418771B	McKinley County NM Crevasse Canyon Formation Channel samples from Green seam, Gibson member, McKinley Mine SE, NW, Sec. 6, T.16N., R.20W.

C 86 D	Underground York Canyon Mine
K 1-5	Nova Scotia
K 2-5	Nova Scotia
C 87 D	Stock pile York Canyon Mine
C 84DD	Navajo Coal Mason Pit Seam 7 Mine grid: N.2,032,700 E.296,700
C 82 DW	Navajo Coal Bighan Pit Seam 8 Mine grid: N. 2,028,500 E. 317,500
C 88 D	York Canyon Coal South Pit York Canyon Mine

Appendix 2A

Proximate Analyses of Study Samples
(Values = percent)

Sample Number	Moisture	VM	FC	Ash	S	FC (dmmf)*	V.M. (dmmf)*
DT519772	1.6	29.5	57.8	11.1	.9	67.12	32.88
DT519771	13.9	25.1	37.9	23.1	.5	62.13	37.87
16727-6	1.21	33.23	47.85	17.71	.6	60.20	39.80
16727-2	10.54	36.94	41.24	11.28	.4	53.44	46.56
NM - TM	1.1	26.3	51.2	21.4	.5	67.7	32.3
16727-1	11.33	37.4	41.23	10.4	.53	53.34	46.66
DT419771	8.8	37.3	40.1	13.8	.36	51.81	48.19
16727-5	12.12	39.91	44.35	3.62	.45	52.89	47.11
16815-2	5.89	37.85	49.70	6.56	3.52	57.75	42.25
16815-1	1.56	34.39	49.58	14.47	.54	59.99	40.01
C - 7	9.1	35.30	42.70	12.90	.4	55.64	44.36
16727-3	11.24	35.87	39.95	12.95	.45	53.51	46.49
418771B	5.6	37.7	46.7	10.0	.5	55.96	44.04
C 86 D	1.8	34.15	54.04	10.02	.50	61.09	38.09
K 1-5	.48	39.98	46.97	12.55	.85	54.72	45.28
K 2-5	.49	34.17	57.57	7.82	.68	63.26	36.74
C 87 D	1.8	32.68	57.88	7.64	.42	62.78	37.22
C 84 DD	9.19	36.94	47.37	6.50	1.20	56.63	43.37
C 82 DW	4.49	40.00	48.90	6.59	.64	55.42	44.58
C 88 D	0.19	33.02	58.78	8.01	.39	64.59	35.41

*Dry mineral matter free fixed carbon content was calculated using the following formula:

Fixed Carbon (dmmf) = FC(100)/ (100 - (M + 1.08A + .55S))

where dmmf = dry mineral matter free

FC = fixed carbon

M = moisture

A = ash content

S = sulfur content

Volatile matter (dmmf) = (100 - FC(dmmf))

Appendix 2B

Proximate Analyses Nomalized to Mineral Matter
(Values = Percent)

Sample Number	Moisture	Volatile Matter	Fixed Carbon	Mineral Matter	Fixed Carbon (dmmf)
DT519772	1.59	29.05	56.90	12.48	66.20
DT519771	13.51	24.41	36.86	25.22	60.12
16727-6	1.18	32.53	46.84	19.45	59.01
16727-2	10.01	36.47	40.72	12.40	52.75
NM - TM	1.07	25.63	49.91	23.39	66.07
16727-1	11.18	36.93	40.71	11.52	52.66
DT419771	8.66	36.74	39.50	15.10	51.81
16727-5	12.05	39.69	44.10	4.16	52.63
16815-2	5.74	36.85	48.39	9.02	56.77
16815-1	1.53	33.81	48.74	15.92	59.04
C - 7	8.97	34.79	42.09	14.15	54.75
16727-3	11.07	35.34	39.36	14.23	52.69
418771B	5.03	37.25	46.14	11.08	55.33
C 86 D	1.78	33.74	53.38	11.10	61.27
K 1-5	0.47	39.45	46.36	13.72	54.03
K 2-5	0.49	33.90	57.05	8.56	62.72
C 87 D	1.78	32.41	57.39	8.42	63.91
C 84 DD	9.12	36.67	47.02	7.19	56.18
C 82 DW	4.45	39.68	48.51	7.36	55.01
C 88 D	0.19	32.73	58.26	8.82	64.03

Moisture, volatile matter and fixed carbon values were normalized by multiplying the as received proximate analyses values by the following correction factor:

$$\text{Correction Factor} = \frac{(100 - MM)}{(100 - A)}$$

where MM = mineral matter

and A = ash content

Appendix 3

Diffractometer Settings Used in Study

Mode: continuous

Recycle: 1

Axis: 2 /

Start angle: 100 degrees

Stop angle: 3 degrees

Scan speed: 4 degree/minute

Full scale: 10,000 CPS (counts per second)

Time construct: 0.1 second

Chart speed: 40 mm/minute

Appendix 4

Sequential Extraction Procedure

General Procedural Statement

Any treatment not requiring heat was carried out in a centrifuge tube fitted with a plastic cap. Supernatant solution and solid material were separated by centrifuging (Sorvall RC-5B Refrigerated Superspeed Centrifuge) at 12000 rpm (revolutions per minute) for 30 minutes; the solution was decanted through Whatman number 5 filter paper. Any particulate matter was rinsed into the centrifuge tube using 10 ml deionized water which served as rinse water. The mixture was centrifuged and decanted as above and the rinse water discarded. Any retained particulate matter was washed into the proper tube using a measured amount of the next leaching solution. Each supernatant solution was stored in a 40 mm. amber pill bottle fitted with a snap cap. Iron was determined with the Varian Techtron, model 1250, using standard atomic absorption methods and settings suggested by the manufacturer. Suggested settings are as follows: (1) the burner height should be 7cm above light path; (2) the slit should be set to 0.2mm; (3) an oxidizing air-acetylene flame should be used; and (4) absorption should be determined at 2483 angstroms. Appropriate solutions were used for zeroing the instrument before determining absorption. Standard curves were drawn before each run. If the curves were non-linear, new standards were prepared using appropriate reagents and iron absorption redetermined. Special blanks were run for procedures 4, 5, and 6. Agitation was by means of a Burrell wrist-action shaker. Chemicals used in the experiment were reagent grade. Solutions were made with deionized water from research Model 1 IonXchanger (Illinois Water Treatment Company). Glassware was rinsed twice in 10% hydrochloric acid before being rinsed with deionized water.

To expedite replication, the procedure will be written up in an instructional format.

Exchangeable Geochemical Phase

Reagents:

Magnesium chloride (1 M pH 7): 204.32g $MgCl_2$ dissolved in 1 liter deionized water; adjust pH to 7 using 50% v/v ammonium hydroxide (NH_4OH).

Ammonium hydroxide- 50% (v/v): carefully mix equal parts NH_4OH and deionized water.

Procedure 1:

1. Add 10 ml 1M magnesium chloride ($MgCl_2$)-pH 7- to each labeled centrifuge tube containing a pre-dried, pre-weighed (weigh by difference) coal sample.

2. Continuously agitate centrifuge tubes for 1 hour at ambient room temperature.

3. Centrifuge samples for 30 minutes at 12,000 rpm (revolutions per minute).

4. Decant the supernatant liquid through Whatman number 5 filter paper into a 40 mm labeled pill bottle and cap bottle.

5. Using 10 ml deionized water, rinse (1) any particulate matter adhearing to the filter paper back into the centrifuge tube and (2) cap and sides of centrifuge tube.

6. Centrifuge and decant as above using a measured amount of the next reagent to rinse any particulate material caught by the filter paper into the centrifuge tube.

7. Using 1M magnesium chloride (pH 7), prepare iron standards having concentrations of 3, 5, 7, and 10 ppm (parts per million).

8. Determine iron absorption using standard atomic absorption methods and settings mentioned in the general statement. Zero the instrument with 1M $MgCl_2$ at pH 7.

Carbonate Geochemical Phase

Reagents:

1 M Sodium acetate (NaOAc), pH 5: Dissolve 136.08g sodium acetate in 1 liter deionized water. Adjust the pH to 5 using acetic acid.
Acetic acid (CH_3COOH), reagent grade

Procedure 2:

1. Add 10 ml 1M sodium acetate, pH 5, to the residue from procedure 1.

2. Continuously agitate for 6 hours at ambient room temperature.

3. Separate supernatant liquid from residue by above procedure (see steps 3,4,5, and 6 above) saving the liquid and discarding the rinse water.

4. Using 1M sodium acetate (pH 5), prepare standards having concentrations of 3, 5, 7, and 10 ppm (parts per million).

5. Zeroing the instrument with 1M sodium acetate (pH 5) determine iron absorbance.

Iron-Oxide Geochemical Phase

Reagents:

25% Acetic Acid (CH_3COOH) v/v: add 250 ml acetic acid to 750 ml deionized water.

0.04M Hydroxylamine hydroxide in 25% (v/v) acetic acid: Dissolve 2.78g NH_2OH-HCl in 1 liter 25% (v/v) acetic acid-the pH is 2.

Procedure 3:

1. Add 20 ml 0.04M hydroxylamine hydroxide in 25% v/v acetic acid to each centrifuge tube containing residual solid from procedure 2.

2. Continuously agitate samples for 8 hours at ambient room temperature.

3. Separate supernatant liquid from residue using above procedure for centrifuging and decanting, saving the decant and discarding the rinse water.

4. Use 30% hydrogen peroxide to rinse any particulate material into the centrifuge tube.

5. Using 0.04M hydroxylamine hydroxide, prepare standards having

concentrations of 3, 5, 7, and 10 ppm.

6. Using 0.04M hydroxylamine hydroxide to zero the instrument, determine iron absorption.

Organic Geochemical Phase

30% Hydrogen peroxide

3.2M Ammonium acetate (NH_4OAc) in 20% v/v nitric acid: Dissolve 246.7g ammonium acetate in 1 liter 20% v/v nitric acid (HNO_3).

3.2M Ammonium acetate in 20% v/v nitric acid diluted to 25% strength: Mix 1 part reagent and 3 parts deionized water.

Procedure 4:

1. Using 5 ml 30% hydrogen peroxide, carefully rinse and police the contents of each centrifuge tube into a labeled 300-ml beaker. Wear rubber gloves and goggles. Cover beaker with a watch glass.
2. Heat mixture at 85 degrees centigrade +/- 2 degrees for 2 hours; agitate every 20 minutes. Add deionized water as necessary to keep from dryness. Use a beaker of water to check temperature if hot plate is not calibrated.
3. After 2 hours, add 3 ml 30% hydrogen peroxide and continue digestion for 3 additional hours. Add deionized water as necessary to keep from dryness. Agitate every 20 minutes.
4. Evidence of black tarry material should completely disappear. The residue should appear clay-like. Color may vary from gray to brown.
5. After oxidation is complete, cool sample.
6. Police and rinse beaker into correct centrifuge tube using 5 ml (3.2M) ammonium acetate in 20% v/v nitric acid. Continue to police and rinse using exactly 15 ml deionized water.
7. Continuously agitate samples for 30 minutes at ambient room temperature.

8. Centrifuge and decant as usual, saving the decant.

9. Using a 25% v/v dilution of 3.2M ammonium acetate in 20% nitric acid. Prepare standard solutions having concentrations of 3,5,7,10,15, and 20 ppm.

10. Using a 25% v/v dilution of 3.2M ammonium acetate in 20% nitric acid to zero the instrument, determine iron concentration by atomic absorption.

Pyrite Geochemical Phase

Reagents:

Hydrochloric acid: reagent grade, 1.19 specific gravity.

Nitric acid: reagent grade

Inverted aqua regia: 3 parts concentrated nitric acid mixed with 1 part concentrated hydrochloric acid.

Procedure 5:

1. Using 15 ml concentrated nitric acid, rinse and police each sample into a labeled 200 ml beaker. Cover with a watch glass.
2. Warm samples on hot plate until temperature reaches 85 degrees centigrade.
3. Carefully add 5 ml concentrated hydrochloric acid and digest for 1 hour.
4. Let samples go to dryness after digestion is completed.
5. Use 20 ml deionized water and 10 ml concentrated hydrochloric acid to rinse and police beaker; filter through Whatman number 41 filter paper into a 100 ml volumetric flask. Bring to volume with deionized water.
6. Use 10% hydrochloric acid to prepare standard solutions having appropriate concentrations.
7. Determine absorption of iron using 10% hydrochloric acid to zero the instrument.
8. Allow ashless filter paper to dry.

Sodium Carbonate Fusion of Residual Material

Reagents:

Sodium carbonate (Na_2CO_3):
Hydrochloric acid: specific gravity 1.19

Procedure 6:

1. Fold dried filter paper and place into a platinum crucible.
2. Heat, to 900 degrees centigrade- raising the temperature slowly in case moisture is present.
3. When combustion complete, take samples from oven.
4. Add from 0.5-1.0 g sodium carbonate (Na_2CO_3), to each sample.
5. Return samples to oven and fuse at 1000 degrees centigrade.
6. Take samples from oven; using platinum tongs, place platinum crucible into a labled beaker containing about 40 ml deionized water; add 10 ml concentrated hydrochloric acid.
7. Using deionized water, police and rinse each crucible 6 times.
8. Transfer beaker contents to a 100 ml volumetric flask. Bring to volume while rinsing beaker with deionzed water.
9. Using 10% hydrochloric acid prepare appropriate standards.
10. Using 10% hydrochloric acid to zero the instrument, determine iron absorbance.

Appendix 4B
Discussion of Reagents

Exchangeable: Discussion of reagent

Tessier et al. state that although ammonium acetate (NH_4OAc, pH 7.0) has been used extensively in soil analyses, unwanted carbonate dissolution has been reported. Tessier et al. (1977) also state that magnesium chloride has no effect on the following geochemical phases: carbonate, silicate, sulfide and organic. Gibbs (1977) additionaly showed that magnesium chloride did not dissolve naturally occurring metallic coatings or organic material.

Carbonate: Discussion of reagent

Grossman and Millet (1961) investigated the selectivity of sodium acetate (NaOAc) adjusted to a pH of 5 using acetic acid and found the reagent dissolved carbonates but did not affect either organic carbon or free iron concentrations after an exposure of nine weeks. Initial investigation by the author showed iron concentration to level off after 6 hours. For this reason an extraction time of 6 hours was decided upon. This finding agreed with that of Tessier.

An additional study of aluminum (Al), silica (Si), and sulfur (S) by Tessier et al. showed that this procedure had no measureable effect on the silicates or sulfides.

Deurer, Forstner and Schmoll (1978) successfully determined total carbonate iron using an acidic-ion exchanger method originally used to remove carbonates from clay and the reader is referred to this article as an alternate method.

Iron Oxide Phase:

The effect of 0.04M hydroxylamine-hydrochloride ($NH_2OH.HCl$) in 25% v/v (volume to volume) acetic acid is to reduce any ferric oxide to its ferrous form. Other reducing reagents used, notably sodium-dithionite-citrate, as cited by Anderson and Jenne (1970), have caused precipitation of sulfides. Gupta and Chen (1975) compared these reagents and found metal concentrations lower, (especially for the least soluble sulfides) when using dithionite-citrate. Since iron sulfide is the least soluble sulfide (K=18.1), no consideration was given this reagent. Tessier et al. (1980) provided information regarding solution-solid contact time and found iron content leveled off after 6-8 hours. This was substantiated in the present study.

Organic Phase:

Gupta and Chen (1975) and Tessier et al.(1979) report the use of nitric acid (HNO_3) to acidify (pH 2) 30% hydrogen peroxide (H_2O_2). Gupta and Chen mention that this combination oxidizes the organics and causes the dissolution of easily dissolved sulfides. Tessier et al. cite that the residual phase contains "resistant" sulfides as well as refractory organic material. The easily dissolved sulfides are amorphous metal sulfides while resistent sulfides are considered to be crystalline metal sulfides (Tessier et al.) Preliminary work showed that a low pH caused dissolution of portions of the residual fraction, for this reason no nitric acid (HNO_3) was used when oxidizing the coal. Deionized water was used in place of nitric (HNO_3) acid to keep the beakers from going to dryness. Samples should not be left unattended, for rapid oxidation may cause actual burning of the coal or excessive formation of carbon dioxide.

Appendix 5A

Exchangeable Geochemical Phase
(Iron concentration in parts per million)

Sample Number	Sample Weight (g)	Volume (ml)	Sample Abs.	Std. Conc.	Std. Abs.	Dilution (if any)	Final Conc.
DT519772	.2521	10	ND				
	.2522	10	ND				
	.2513	10	ND				
DT519771	.2512	10	ND				
	.2500	10	ND				
	.2510	10	ND				
16727-6	.2504	10	ND				
	.2506	10	ND				
	.2514	10	ND				
16727-2	.2500	10	ND				
	.2500	10	ND				
	.2500	10	ND				
NM-TM	.2500	10	ND				
	.2500	10	ND				
	.2500	10	ND				
NBS 1635	.2500	10	ND				
	.2505	10	ND				
	.2500	10	ND				

Standard Solution Information

Standard Concentration	Standard Absorbance
1	44
2	86
3	133
5	213
7	296
10	388

Appendix 5A
(Continued)
Exchangeable Geochemical Phase
(Iron concentration in parts per million)

Sample Number	Sample Weight (g)	Volume (ml)	Sample Abs.	Std. Conc.	Std. Abs.	Dilution (if any)	Final Conc.
16726-1	.1504	10	ND				
	.1675	10	ND				
	.1992	10	ND				
DT419771	.1882	10	7	0.5	13		14
	.1389	10	14	0.5	13		38.8
	.1989	10	13	.5	13		25.1
16727-5	.2105	10	ND				
	.2060	10	ND				
	.1790	10	ND				
16812-2	.2038	10	231	7.	211	1/10	3760
	.2265	10	277	10	304	1/10	4023
	.2290	10	348	10	304	1/10	4999
16815-1	.1825	10	ND				
	.2242	10	ND				
	.1742	10	ND				
C - 7	.2358	10	ND				
	.1334	10	ND				
	.1726	10	ND				
16727-3	.1489	10	ND				
	.1840	10	ND				
	.1746	10	ND				
418771B	.1873	10	ND				
	.1729	10	ND				
	.1858	10	ND				

Standard Solution Information

Standard Concentration	Standard Absorbance
0.5	13
1.5	44
3.0	83
5.0	156
7.0	211
10.0	304

Appendix 5A
(Continued)
Exchangeable Geochemical Phase
(Iron concentration in parts per million)

Sample Number	Sample Weight (g)	Volume (ml)	Sample Abs.	Std. Conc.	Std. Abs.	Dilution (if any)	Final Conc.
C 86 D	.1151	5	ND				
	.1015	5	ND				
	.1139	5	ND				
K 1-5	.1017	5	92	3	83		163.5
	.1009	5	97	3	83		173.7
	.1032	5	99	3	83		173.4
K 2-5	.1293	5	29	1.5	44		38.2
	.1154	5	31	1.5	44		45.7
	.1120	5	37	1.5	44		56.3
C 87 D	.1360	5	ND				
	.1031	5	ND				
	.1101	5	ND				
C 84 DD	.1077	5	177	5	156		263.4
	.1130	5	150	5	156		212.7
	.1139	5	157	5	156		226.7
C 82 DW	.1255	5	31	1.5	44		42.1
	.1043	5	23	1.5	44		37.6
	.0714	5	22	1.5	44		59.3
C 88 D	.1419	5	ND				
	.0983	5	ND				
	.0973	5	ND				
NBS 1635	.1024	5	48	1.5	44		79.9
	.1027	5	46	1.5	44		76.3
	.1084	5	46	1.5	44		72.3

Standard Solution Information

Standard Concentration	Standard Absorbance
0.5	13
1.5	44
3.	83
5.	156
7.	211
10	304

Appendix 5B
Carbonate Geochemical Phase
(Iron Concentration in parts per million)

Sample Number	Sample Weight (g)	Volume (ml)	Sample Abs.	Std. Conc.	Std. Abs.	Dilution (if any)	Final Conc.
DT519772	.2521	8	170	5	213		137.5
	.2522	8	208	5	213		154.8
	.2513	8	189	5	213		141.2
DT519771	.2512	8	ND				
	.2500	8	ND				
	.2510	8	ND				
16727-6	.2504	8	79	2	86		58.7
	.2506	8	78	2	86		57.9
	.2514	8	77	2	86		57.0
16727-2	.2500	8	ND				
	.2500	8	ND				
	.2505	8	ND				
NM-TM	.2500	8	15	1	44		10.9
	.2500	8	14	1	44		10.2
	.2500	8	15	1	44		10.9
NBS1635	.2500	8	ND				
	.2505	8	ND				
	.2500	8	ND				

Standard Solution Information

Standard Concentration	Standard Absorbance
1	44
2	86
3	133
5	213
7	296
10	388

Appendix 5B
(Continued)
Carbonate Geochemical Phase
(Iron concentration in parts per million)

Sample Number	Sample Weight (g)	Volume (ml)	Sample Abs.	Std. Conc.	Std. Abs.	Dilution (if any)	Final Conc.
16727-1	.1504	10	ND				
	.1675	10	ND				
	.1992	10	ND				
DT419771	.1882	10	ND				
	.1389	10	ND				
	.1989	10	ND				
167227-5	.2105	10	ND				
	.2060	10	ND				
	.1790	10	ND				
16815-2	.2030	10	60	2	58		101.5
	.2265	10	89	3	94		125.4
	.2290	10	70	2	58		105.4
16815-1	.1825	10	28	1	28		54.8
	.2242	10	56	2	58		86.1
	.1742	10	35	1.5	39		77.3
C - 7	.2358	10	ND				
	.1334	10	ND				
	.1726	10	ND				
16727-3	.1489	10	ND				
	.1840	10	ND				
	.1746	10	ND				
418771B	.1873	10	18				
	.1729	10	4				
	.1858	10	8				

Standard Solution Information	Standard Concentration	Standard Absorbance
	.5	10
	1.0	28
	1.5	39
	3.0	94
	5.0	165
	7.0	265
	10.0	353

Appendix 5B
(Continued)
Carbonate Geochemical Phase
(Iron concentration in parts per million)

Sample Number	Sample Weight (g)	Volume (ml)	Sample Abs.	Std. Conc.	Std. Abs.	Dilution (if any)	Final Conc.
C 86 D	.1151	10	20	1.0	28		62
	.1015	10	17	.5	10		83.7
	.1139	10	8	.5	10		35
K 1-5	.1017	10	7	.5	10		
	.1009	10	3	.5	10		
	.1032	10	2	.5	10		
K 2-5	.1293	10	ND				
	.1154	10	ND				
	.1120	10	ND				
C 87 D	.1360	10	52	2.0	58		131.8
	.1031	10	38	1.5	39		141.7
	.1101	10	33	1.0	28		107.0
C 84 DD	.1077	10	ND				
	.1130	10	ND				
	.1139	10	ND				
C 82 DW	.1255	10	ND				
	.1043	10	ND				
	.0714	10	ND				
C 88 D	.1419	10	ND				
	.0983	10	ND				
	.0973	10	ND				
NBS1635	.1024	10	ND				
	.1027	10	ND				
	.1084	10	ND				

Standard Solution Information

Standard Concentration	Standard Absorbance
0.5	10
1.0	28
1.5	39
2.0	58
3.0	94
5.0	165
7.0	265
10.0	353

Appendix 5C
Iron Oxide Geochemical Phase
(Iron Concentration in parts per million)

Sample Number	Sample Weight (g)	Volume (ml)	Sample Abs.	Std. Conc.	Std. ABS.	Dilution (if any)	Final Conc.
DT519772	.3105	20	306	10	268	-	735.0
	.3394	20	360	10	268	-	791.0
	.3333	20	330	10	268	-	739.0
DT519771	.3055	20	349	10	268	1/2	1705.0
	.3720	20	348	10	268	1/2	1396.0
	.3655	20	331	10	268	1/2	1351.0
16727-6	.3594	20	144	5	147	1/2	545.0
	.4077	20	142	5	147	1/2	474.0
	.3328	20	131	5	131	1/2	536.0
16727-2	.2647	20	70	3	84	1/3	567.0
	.2830	20	120	5	147	1/2	577.0
	.3365	20	147	5	147	-	594.0
NM-TM	.3616	20	197	7	193	-	395.2
	.3128	20	245	7	193	-	584.5
	.3460	20	214	7	193	-	528.4
NBS1635	.3420	20	154	5	147	-	306.0
	.2662	20	133	5	147	-	340.0
	.3171	20	151	5	147	-	324.0

Standard Solution Information

Standard Concentration	Standard Absorbance
3	84
5	147
7	193
10	268

Appendix 5C
(Continued)
Iron Oxide Geochemical Phase
(Iron concentration in parts per million)

Sample Number	Sample Weight (g)	Volume (ml)	Sample Abs.	Std. Conc.	Std. Abs.	Dilution (if any)	Final Conc.
16727-1	.1504	20	79	3	89		354.1
	.1675	20	81	3	89		326.
	.1992	20	98	3	89		331.7
DT419771	.1882	20	23	1.5	25		146.7
	.1389	20	20	1.5	25		172.8
	.1989	20	26	1.5	25		156.9
16727-5	.2105	20	31	3	38		155.0
	.2060	20	28	1.5	25		163.1
	.1790	20	28	1.5	25		187.7
16815-2	.2038	20	66	3	89		218.3
	.2265	20	130	5	139		412.9
	.2290	20	91	3	89		267.9
16815-1	.1825	20	84	3	89		310.3
	.2242	20	109	3	89		327.8
	.1742	20	77	3	89		298.0
C - 7	.2358	20	41	2	38		183.0
	.1334	20	31	1.5	25		278.9
	.1726	20	38	2	38		231.7
16727-3	.1489	20	59	3	89		267.1
	.1840	20	61	3	89		223.5
	.1746	20	57	3	89		220.1
418771B	.1873	20	120	5	139		460.9
	.1729	20	123	5	139		511.8
	.1858	20	112	5	139		433.7

Standard Solution Information

Standard Concentration	Standard Absorbance
1.0	12
1.5	25
2.0	38
3	89
5	139
7	196
10	284

Appendix 5C
(Continued)
Iron Oxide Geochemical Phase
(Iron concentration in parts per million)

Sample Number	Sample Weight (g)	Volume (ml)	Sample Abs.	Std. Conc.	Std. Abs.	Dilution (if any)	Final Conc.
C 86 D	.1151	20	220	5	243		786.6
	.1015	20	198	3	161		726.9
	.1139	20	187	3	161		611.8
K 1-5	.1017	20	43	1	48		176.2
	.1009	20	38	.5	22		171.2
	.1032	20	35	.5	22		154.2
K 2-5	.1293	20	12	.5	22		42.2
	.1154	20	13	.5	22		51.2
	.1120	20	13	.5	22		52.8
C 84 DD	.1077	20	94	1.5	78		335.7
	.1130	20	100	1.5	78		340.4
	.1139	20	110	1.5	78		371.4
C 82 DW	.1255	20	33	.5	22		119.5
	.1043	20	26	.5	22		113.3
	.0714	20	22	.5	22		140.0
C 88 D	.1419	20	155	3	161		407.1
	.0983	20	122	3	161		462.5
	.0973	20	120	3	161		459.6
NBS1635	.1024	20	97	1.5	78		333.1
	.1027	20	99	1.5	78		370.8
	.1084	20	122	1.5	78		432.9

Standard Solution Information

Standard Concentration	Standard Absorbance
.5	22
1.0	48
1.5	78
3	161
5	243
7	342
10	495

Appendix 5D
Organic Geochemical Phase
(Iron concentrations in parts per million)

Sample Number	Sample Weight (g)	Volume (ml)	Sample Abs.	Std. Conc.	Std. Abs.	Dilution (if any)	Final Conc.
DT519772	.2521	20	154	1.5	112		163.6
	.2522	20	61	1.5	112		64.8
	.2513	20	120	1.5	112		127.9
DT519771	.2512	20	464	7	498	1/2	1039
	.2500	20	474	7	498	1/2	1066
	.2510	20	494	7	498	1/2	1106
16727-6	.2504	20	422	7	498		473.8
	.2504	20	-	-	-		-
	.2514	20	441	7	498		493.
16727-2	.2500	20	165	1.5	112		176.8
	.2500	20	204	3	232		211
	.2505	20	229	3	232		236
MN-TM	.2500	20	249	3	232		257.6
	.2500	20	345	5	370		373
	.2500	20	492	7	498		553.2
NBS1635	.2500	20	98	1.5	112		105
	.2505	20	151	1.5	112		161
	.2500	20	255	3	232		264

Standard Solution Information

Standard Concentration	Standard Absorbance
1.5	112
3	232
5	370
7	498
10	674

Appendix 5D
(Continued)
Organic Geochemical Phase
(Iron concentration in parts per million)

Sample Number	Sample Weight (g)	Volume (ml)	Sample Abs.	Std. Conc.	Std. Abs.	Dilution (if any)	Final Conc.
16727-1	.1504	20	89	2	89		266
	.1675	20	103	2.5	111		277
	.1992	20	96	2	89		216.6
DT419771	.1882	20	72	1.5	65		176.6
	.1389	20	48	1.0	43		160.7
	.1989	20	67	1.5	65		155.5
16727-5	.2105	20	38	1.0	43		84
	.2060	20	50	1.0	43		112.9
	.1790	20	31	.5	20		86.6
16815-2	.2038	20	115	2.5	111		254.2
	.2265	20	124	3	134		245.1
	.2290	20	167	3	134		326.5
16815-1	.1825	20	62	1.5	65		156.8
	.2242	20	123	2.5	111		247.1
	.1742	20	115	2.5	111		297.4
C - 7	.2358	20	23	.5	20		48.8
	.1334	20	40	1.0	43		149.9
	.1726	20	46	1.0	43		123.9
16727-3	.1489	20	75	1.5	65		232.5
	.1840	20	46	1.0	43		116.3
	.1746	20	77	1.5	65		203.5
418771B	.1873	20	348	7	293		887.8
	.1729	20	89	2	89		231.3
	.1858	20	43	1.0	43		107.6

Appendix 5D
(Continued)
Organic Geochemical Phase
(Iron Concentration in parts per million)

Sample Number	Sample Weight (g)	Volume (ml)	Sample Abs.	Std. Conc.	Std. Abs.	Dilution (if any)	Final Conc.
C 86 D	.1151	20	234	5	202		1006
	.1015	20	82	1.5	62		390.9
	.1139	20	76	1.5	62		322.9
K 1-5	.1017	20	53	1.5	62		252.2
	.1009	20	24	.5	21		113.3
	.1032	20	13	.5	21		59.9
K 2-5	.1293	20	27	.5	21		99.4
	.1154	20	10	.5	21		41.
	.1120	20	13	.5	21		55.3
C 87 D	.1360	20	124	3.	125		437.6
	.1031	20	62	1.5	62		290.9
	.1101	20	63	1.5	62		276.9
C 84 DD	.1077	20	45	1.5	62		202.2
	.1130	20	41	1.5	62		175.5
	.1139	20	52	1.5	62		220.9
C 82 DW	.1255	20	47	1.5	62		181.2
	.1043	20	53	1.5	62		245.9
	.0714	20	29	.5	21		193.4
C 88 D	.1419	20	74	1.5	62		252.3
	.0983	20	47	1.5	62		231.4
	.0973	20	40	1.5	62		198.9
NBS 1635	.1024	20	78	1.5	62		368.6
	.1027	20	20	.5	21		92.7
	.1084	20	82	1.5	62		366.0

Standard Solution Information

Standard Concentration	Standard Absorbance
.5	21
1.5	62
3.	125
5.	202
7.	288
10.	408

Appendix 5E
Pyritic Geochemical Phase
(Iron concentration in parts per million)

Sample Number	Sample Weight (g)	Volume (ml)	Sample Abs.	Std. Conc.	Std. Abs.	Dilution (if any)	Final Conc.
DT519772	.2521	100	579	10(A)	622		3692.5
	.2522	100	526	10(A)	622		3353.1
	.2513	100	611	10(A)	622		3908.9
DT519771	.2512	50	388	5(A)	334	1/5	5780.6
	.2500	100	658	7(C)	611	1/2	6031.0
	.2510	100	594	7(C)	611	1/2	5422.5
16527-6	.2504	100	322	5(A)	334	1/2	3850.0
	.2506	100	300	5(A)	334	1/2	3584.0
	.2514	100	342	5(A)	334	1/2	4073.0
16726-2	.2500	100	538	7(B)	580		2597.0
	.2500	100	402	7(A)	460		2446.0
	.2505	100	422	7(A)	460		2563.0
NM-TM	.2500	100	276	5(A)	334	1/5	8263.0
	.2500	100	265	5(A)	334	1/5	7934.0
	.2500	100	231	5(A)	334	1/5	6916.0
NBS1635	.2500	100	208	3(A)	209		1194
	.2505	100	267	3(A)	209		1530
	.2500	100	243	3(A)	209		1395

Standard Solution Information

	Std. Conc.	Std. Abs.		Std. Conc.	STd. Abs.		Std. Conc.	Std. Abs.
A =	3	209	B =	3	272	C =	3	296
	5	334		5	432		5	463
	7	460		7	580		7	611
	10	622		10	760		10	798

Appendix 5E
(Continued)
Pyritic Geochemical Phase
(Iron Concentration in parts per million)

Sample Number	Sample Weight (g)	Volume (ml)	Sample Abs.	Std. Conc.	Std. Abs.	Dilution (if any)	Final Conc.
16727-1	.1504	20	111	3	136	1/10	3256
	.1675	20	108	3	136	1/10	2845
	.1992	20	148	3	136	1/10	3278
DT419771	.1882	20	242	5	215	1/5	2990
	.1389	20	185	5	215	1/5	3097
	.1989	20	311	7	304	1/5	3600
16727-5	.2105	20	404	10	386		994
	.2060	20	386	10	386		971
	.1790	20	462	10	386		1337
16815-2	.2038	20	341	7	304	1/10	7706
	.2265	20	382	10	420	1/10	8031
	.2290	20	398	10	420	1/10	8276
16815-1	.1825	20	177	5	215	1/10	4511
	.2242	20	191	5	215	1/10	3962
	.1742	20	158	3	136	1/10	4002
C - 7	.2358	20	270	5	215	1/10	5326
	.1334	20	156	3	136	1/10	5159
	.1726	20	196	5	215	1/10	5282
16727-3	.1489	20	193	5	215	1/5	3014
	.1840	20	220	5	215	1/5	2781
	.1746	20	200	5	215	1/5	2664
418771B	.1873	20	112	3	136	1/5	1319
	.1729	20	166	3	136	1/5	2118
	.1859	20	211	5	215	1/5	2641

Standard Solution Information

Standard Concentration	Standard Absorbance
3	136
5	215
7	304
10	420

Appendix 5E
(continued)
Pyritic Geochemical Phase
(Iron concentration in parts per million)

Sample Number	Sample Weight (g)	Volume (ml)	Sample Abs.	Std. Conc.	Std Abs.	Dilution (if any)	Final Conc.
C 86 D	.1151	20	141A	5	125	1/5	4952
	.1015	20	156A	7	172	1/5	6207
	.1139	20	110A	5	125	1/5	3424
K 1-5	.1017	20	189A	7	172	1/2	3029
	.1009	20	150A	7	172	1/2	2458
	.1032	20	146A	7	172	1/2	2287
K 2-5	.1293	20	275A	10	242		1763
	.1154	20	-	-			
	.1120	20	277A	10	242		2054
C 87 D	.1360	20	456B	10	461	1/2	2897
	.1031	20	409B	10	461	1/2	3317
	.1101	20	370B	7	303	1/2	2870
C 84 DD	.1077	20	274B	5	244	1/2	2136
	.1130	20	305C	7	286	1/2	2619
	.1139	20	222C	5	211	1/2	1879
C 82 DW	.1255	20	281C	7	286	1/2	-
	.1043	20	288C	7	86	1/2	2665
	.0714	20	277C	7	286	1/2	3764
C 88 D	.1419	20	400C	10	408	1/2	2763
	.0983	20	310C	7	286	1/2	3072
	.0973	20	299C	7	286	1/2	2980
NBS1635	.1024	20	282C	7	286		1328
	.1027	20	374C	10	408		1781
	.1084	20					1365

Standard Solution Information

A - Std. Conc.	Std. Abs. ppm.	B - Std. Conc.	Std. Abs. ppm.	C - Std. Conc.	Std. Abs. ppm.
3	78	3	153	3	130
5	125	5	244	5	211
7	172	7	303	7	286
10	242	10	461	10	408

Appendix 5F
Iron Recovered After Sodium Carbonate Fusion
(Iron concentration in parts per million)

Sample Number	Sample Weight (g)	Volume (ml)	Sample Abs.	Std. Conc.	Std. Abs.	Dilution (if any)	Final Conc.
DT519772	.2521	100	44	.5	40		218
	.2522	100	10	.5	40		49.5
	.2513	100	100	-	-		ND
DT519771	.2512	100	100	1.5	119		501.8
	.2500	100	114	1.5	119		574.8
	.2510	100	spilled				
16727-6	.2504	100	198	3	227		1045
	.2506	100	185	3	227		975.6
	.2514	100	147	1.5	119		737
16727-2	.2500	100	7	.5	40		35
	.2500	100	270	3	227		1427
	.2505	100	ND	-	-		ND
NM-TM	.2500	100	-	-	-		-
	.2500	100	138	1.5	119		695
	.2500	100	-	-	-		ND
NBS1635	.2500	100	191	3.0	227		1010
	.2505	100	102	1.5	119		513
	.2500	100	143	1.5	119		721

Standard Solution Information

Standard Concentration	Standard Absorbance
.5	40
1.5	119
3.0	227
5.0	350
7.0	491
10.0	650

Appendix 5F
(Continued)
Iron Recovered After Sodium Carbonate Fusion
(Iron concentration in parts per million)

Sample Number	Sample Weight (g)	Volume (ml)	Sample Abs.	Std. Conc.	Std. Abs.	Dilution (if any)	Final Conc.
16727-1	.1504	20	77	3	93		330.
	.1675	20	46	1	30		183
	.1992	20	110	3	93		356
DT419771	.1882	20	59	1	30		209
	.1389	20	54	1	30		259
	.1989	20	67	3	93		217
16727-5	.2105	20	20	1	30		61
	.2060	20	17	1	30		53
	.1790	20	91	3	93		328
16815-2	.2038	20	181	5	152		584
	.2265	20	231	7	209		683
	.2290	20	241	7	209		705
16815-1	.1825	20	116	3	93		410
	.2242	20	301	10	313		858
	.1742	20	216	7	209		792
C - 7	.2358	20	210	7	209		597
	.1334	20	281	7	209		959
	.1726	20	262	7	209		1017
16727-3	.1489	20	199	7	209		895
	.1840	20	78	3	93		274
	.1746	20	-	-	-		-
418771B	.1873	20	113	3	93		389
	.1729	20	51	1	30		153
	.1858	20	63	3	93		219

Standard Solution Information

Standard Concentration	Standard Absorbance
1	30
3	93
5	152
7	209
10	313

Appendix 5F
(Continued)
Iron Recovered After Sodium Carbonate Fusion
(Iron concentration in parts per million)

Sample Number	Sample Weight (g)	Volume (ml)	Sample Abs.	Std. Conc.	Std. Abs.	Dilution (if any)	Final Conc.
C 86 D	.1151	20	84	3	114		410
	.1015	20	39	3	114		200
	.1139	20	12	3	114		53
K 1-5	.1017	20	5	3	114		23
	.1009	20	29	3	114		149
	.1032	20	14	3	114		69
K 2-5	.1293	20	30	3	114		120
	.1154	20	-	-			ND
	.1120	20	-	-			ND
C 87 D	.1360	20	9	3	114		33
	.1031	20	-	-			ND
	.1101	20	18	3	114		84
C 84 DD	.1077	20	73	3	114		531
	.1130	20	43	3	114		297
	.1139	20	40	3	114		411
C 82 DW	.1255	Spilled					
	.1043	20	94	3	114		507
	.0714	20	-				ND
C 88 D	.1419	20	-				ND
	.0983	20	74	3	114		272
	.0973	20	30	3	114		160
NBS 1635	.1024	20	-				ND
	.1027	20	-				ND
	.1084	20	52	3	114		250

Standard Solution Information	Standard Concentration	Standard Absorbance
	3	114
	5	177
	7	242
	10	336

Appendix 6: Parts A, B, and C
Mean and Total Iron Values Determined for the Study Samples

Part 6A

Mean iron value in parts per million for the: (1) exchangeable geochemical fraction; (2) carbonate geochemical fraction; (3) iron-oxide geochemical fraction; (4) organic geochemical fraction; and (5) pyrite fraction. Standard deviation is given in parts per million.

Sample Number	Exchangeable Fraction	Carbonate Fraction	Iron Oxide Fraction	Organic Fraction	Pyrite* Fraction
DT519772	ND	145+/-9	755+/-31	146+/-25	3740+/- 94
T519771	ND	ND	1374+/-60	1070+/-34	6444+/-108
16727-6	ND	58+/-1	518+/-38	484+/-13	4755+/-88
16727-2	ND	ND	579+/-10	208+/-30	2547+/-64
NM-TM	ND	11+/-0.5	503+/-24	395+/-149	7933+/-864
16727-1	ND	ND	329+/-4	272+/-8	3610+/-30
DT419771	ND	ND	152+/-7	159+/-4	3270+/-110
16727-5	ND	ND	168+/-17	86+/-2	1040+/-20
16815-2	4261+/-653	111+/-13	243+/-35	275+/-64	8661+/-340
16815-1	ND	72+/-12	312+/-15	272+/-35	4782+/-17
C -7	ND	ND	231+/-48	137+/-18	6115+/-180
16727-3	ND	ND	237+/-26	181+/-61	3964+/-940
418771B	ND	ND	448+/-19	169+/-87	1989+/-390
C 86 D	170+/-6	73+/-16	757+/-42	357+/-48	5882+/-724
K1-5	46+/-9	ND	174+/-4	142+/-99	2466+/-185
K2-5	ND	ND	49+/-6	65+/-30	1978+/-107
C 87 D	ND	137+/-7	934+/-6	353+/-126	2916+/-26
C 84 DD	220+/-10	ND	338+/-3	212+/-13	2809+/-140
C 82 DW	40+/-3	ND	117+/-5	207+/-49	3474+/-410
C 88 D	ND	ND	461+/-1	242+/-15	2941+/-250
NBS1635	76+/-4	ND	352+/-27	368+/-2	1476+/-209
NBS1635	ND	ND	323+/-30	177+/-86	2118+/-200

*Pyrite iron equals iron recovered during pyrite oxidation plus iron recovered after the sodium carbonate fusion.

Appendix 6B
Mean Total Iron Content

Sample Number	Total Iron Content
DT519772	4786+/-207
DT519771	8888+/-169
16727-6	5815+/-205
16727-2	3334+/-118
NM-TM	8842+/-256
16727-1	4211+/-28
DT419771	3581+/-110
16727-5	1294+/-24
16815-2	13551+/-302
16815-1	5438+/-68
C-7	6483+/-187
16727-3	4382+/-942
418771B	2606+/-618
C 86 D	7239+/-727
K1-5	2828+/-210
K2-5	2092+/-111
C 87 D	4340+/-129
C 84 DD	3579+/-141
C 82 DW	3838+/-413
C 88 D	3644+/-250
NBS1635	2272+/-211
NBS1635	2618+/-230

Appendix 6C

Mean iron content as percent total iron for the: (1) exchangeable geochemical fraction; (2) carbonate geochemical fraction; (3) iron-oxice geochemical fraction; (4) organic geochemical fraction; and (5) pyrite fraction.

Sample Number	Exchangeable Fraction	Carbonate Fraction	Iron-Oxide Fraction	Organic Fraction	Pyrite Fraction
DT519772	0	3	16	3	78
DT519771	0	0	15.5	12	72.5
16727-6	0	1	9	8	82
16727-2	0	0	17	6.5	76.5
NM-TM	0	0.1	7.9	4.5	90
16727-1	0	0	5.6	6	86
DT419771	0	0	4	4	91
16727-5	0	0	13	7	80
16815-2	31	1	2	2	64
16815-1	0	1	6	5	88
C - 7	0	0	4	2	94
16727-3	0	0	5	4	90
418771B	0	0	17	5	76
C 86 D	2	1	10	6	81
K 1-5	1	0	7	5	87
K 2-5	0	0	2	3	95
C 87 D	0	3	22	8	67
C 84 DD	6	0	10	6	78
C 82 DW	1	0	3	5	91
C 88	0	0	13	7	81

Appendix 7

Distribution coefficient K and values used to calculate this coefficient.

Sample Number	(VM+FC)	$\frac{\text{Organic Iron}}{\text{(VM+FC)}}$	Percent Pyrite	(MM-PY)	$\frac{\text{Oxides Iron}}{\text{(MM-Py)}}$	K*
DT519772	85.95	1.7E-04	0.8014	11.67	6.47E-03	38.06
DT519771	61.27	1.75E-03	1.3808	23.84	5.76E-03	3.29
16727-6	79.37	6.10E-04	1.0189	18.43	2.81E-03	4.61
16727-2	77.19	2.69E-04	0.5458	11.85	4.89E-03	18.16
NM - TM	75.54	5.23E-04	1.6999	21.69	2.67E-03	5.10
16727-1	77.64	3.50E-04	0.774	10.75	3.06E-03	8.74
DT419771	76.24	2.09E-04	0.701	14.40	1.10E-03	5.26
16727-5	83.79	1.03E-04	0.223	3.94	4.27E-03	41.46
16815-2	85.24	3.23E-04	1.856	7.16	3.39E-03	10.49
16815-1	82.55	3.29E-04	1.025	14.90	2.09E-03	6.35
C - 7	76.88	1.78E-04	1.310	12.84	1.80E-03	10.11
16727-3	74.70	2.42E-04	0.849	13.38	1.77E-03	7.31
418771B	83.39	2.03E-04	0.426	10.65	4.20E-03	20.69
C 86 D	87.12	4.10E-04	1.261	9.84	7.69E-03	18.16
K 1-5	85.81	1.65E-04	0.528	13.49	1.29E-03	7.82
K 2-5	90.95	7.15E-05	0.424	8.44	5.81E-04	7.24
C 87 D	89.80	3.93E-04	0.625	7.86	1.19E-02	30.28
C 84 DD	83.69	2.53E-04	0.602	7.08	4.78E-03	18.89
C 82 DW	88.19	2.35E-04	0.744	6.73	1.74E-03	7.40
C 88 D	90.99	2.66E-04	0.630	8.24	5.60E-03	21.05

*The distribution coefficient, K, is equal to the concentration of the iron within the iron-oxide phase divided by the concentration of organic iron within the hydrocarbon phase.

Appendix 8: Parts A, B. and C

Distribution Coefficients for Gluskoter's Whole Coal Selections and Values Used to Calculate the Coefficients.

Part A

Values Used to Calculate the Concentration of Organic Iron Within the Hydrocarbon Phase

Sample Number	VM*	FC#	(VM + FC)	$\frac{\text{ORGFE}}{\text{(VM + FC)}}$
C16543	41.69	43.73	85.42	1.08E-04
C17001	38.06	46.92	84.98	6.80E-05
C18304	39.04	46.85	85.89	7.45E-05
C18560	39.17	39.55	78.72	8.38E-05
C18816	38.16	51.57	89.73	6.69E-05
C18820	16.34	70.79	87.13	8.26E-05
C18841	40.81	45.41	86.22	2.81E-05
C18848	19.72	67.44	87.16	6.2E-05
C18857	38.01	44.22	82.23	8.15E-05
C19000	42.58	49.52	92.10	2.44E-04
C18844	24.94	54.81	89.75	1.63E-04
C18824	24.27	61.69	85.96	5.35E-05
C18440	39.23	49.91	89.14	2.47E-05
C18320	37.29	45.87	83.16	6.61E-05
C18368	38.32	45.26	83.58	5.98E-05
C18445	40.93	50.51	91.44	3.28E-05
C18457	48.49	44.43	93.22	6.03E-05
C14684	37.21	50.45	87.66	1.39E-04
C15999	36.78	48.01	84.79	8.85E-05

*Volatile matter normalized to mineral matter.

#Fixed carbon normalized to mineral matter.

(Refer to text for original data)

Part 8B

Values used to calculate the concentration of non-pyritic inorganic iron within the mineral matter minus pyrite phase.

Sample Number	PYFE (percent)	NON-PY* INORGFE (percent)	PY (percent)	(MM-PY) (percent)	NON-PY INORGFE / (MM - PY)
C16543	1.05	0.531	2.25	12.33	4.30E-02
C17001	2.29	0.464	4.91	10.11	4.59E-02
C18304	2.30	0.480	4.93	9.18	5.23E-02
C18560	3.99	1.233	8.55	12.83	9.61E-02
C18816	0.47	0.124	1.01	9.26	1.34E-02
C18820	0.23	0.325	0.49	12.37	2.63E-02
C18841	2.17	0.656	4.65	9.13	4.76E-02
C18848	0.04	0.660	0.08	12.86	5.12E-02
C18857	2.20	0.673	4.71	13.06	5.16E-02
C19000	0.07	0.308	0.15	7.75	3.96E-02
C18844	1.00	0.287	2.14	8.11	3.54E-02
C18824	0.38	0.229	0.81	13.23	1.73E-02
C18440	0.01	0.319	0.02	10.84	2.94E-02
C18320	1.60	0.205	3.43	13.51	1.51E-02
C18368	1.61	0.485	3.45	12.97	3.74E-02
C18445	0.20	0.176	0.43	8.13	2.16E-02
C18457	0.15	0.055	0.32	6.76	8.20E-03
C14684	1.26	0.198	2.70	9.64	2.05E-02
C15999	1.57	0.473	3.36	11.85	3.99E-02

*Non-pyritic inorganic iron content equals total iron content minus organic iron content and pyrite iron content.

Part 8C

Distribution coefficients labeled K.

Sample Number	K*
C16543	398.1
C17001	675.0
C18304	702.0
C18560	1147.2
C18816	200.3
C18820	318.4
C18841	169.4
C18848	825.8
C18857	632.6
C19000	162.3
C18844	217.2
C18824	323.4
C18440	1190.3
C18320	228.4
C18368	625.4
C18445	658.5
C18457	136.0
C14684	147.8
C15999	450.5

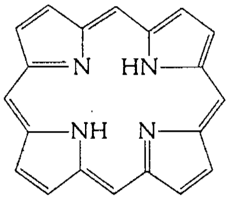
*K equals the concentration of the non-pyritic iron within the mineral matter minus pyrite phase divided by the concentration of organic iron within the hydrocarbon phase.

Appendix 9

Metallo-organic complexes

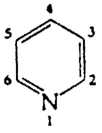
The following discussion is bases upon information presented by Pine et at. (1980). The figures are taken from Pine's Organic Chemistry (1980).

Iron (Co, Ni Mg. and others) may be incorporated into an organic molecule; such a molecule is known as a metallo-organic! complex. Another well used term for such a molecule is chelate- the metal haven been chelated. Acturally chelated molecules belong to a group of biologically important compounds correctly termed metalloporphyrins (hemoglobin and chlorophyll both belong to this group). The parent structure is an organic molecule called porphin, a cyclic compound composed of four pyrrole (C4H5N) rings connected by methine bridges as shown below (p. 642, Pine et al., 1980)

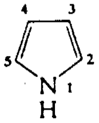


Porphin

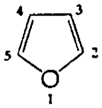
Pyrrole is a heterocyclic (cyclic compounds having at least 1 non-carbon ring member) aromatic compound (special group of cyclic compounds, usually a 6 member ring, having alternate single and couble bounds which are responsible for distinctive chemical and physical properties) which has 1 nitrogen atom within its ring structure. Other coal tar heterocyclics are shown for interest's sake (p. 673, Pine et al, 1980).



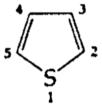
Pyridine



Pyrrole

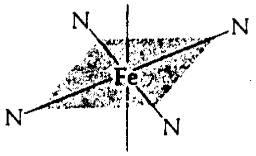


Furan



Thiophene

Porphyrins are differentiated according to which groups are substituted on the pyrrole rings as well as by the complexing metal. The metal atom is held in the center of a porphyrin by coordination with the nitrogen atoms of the pyrrole ring (p. 542, Pine et at, 1980). (The coordination number gives the number of groups connected to a given atom. It does not have to be the same as valence due to formation of multiple bonds between atoms in many compounds.) When iron is bonded to the four nitrogen atoms, the porphyrin's geometry is that of a square and is planar (as shown below). However, it may become non-planar if the fifth or sixth coordination site for iron serves as the bonding site for these are above and below the plane of the porphyrin ring.



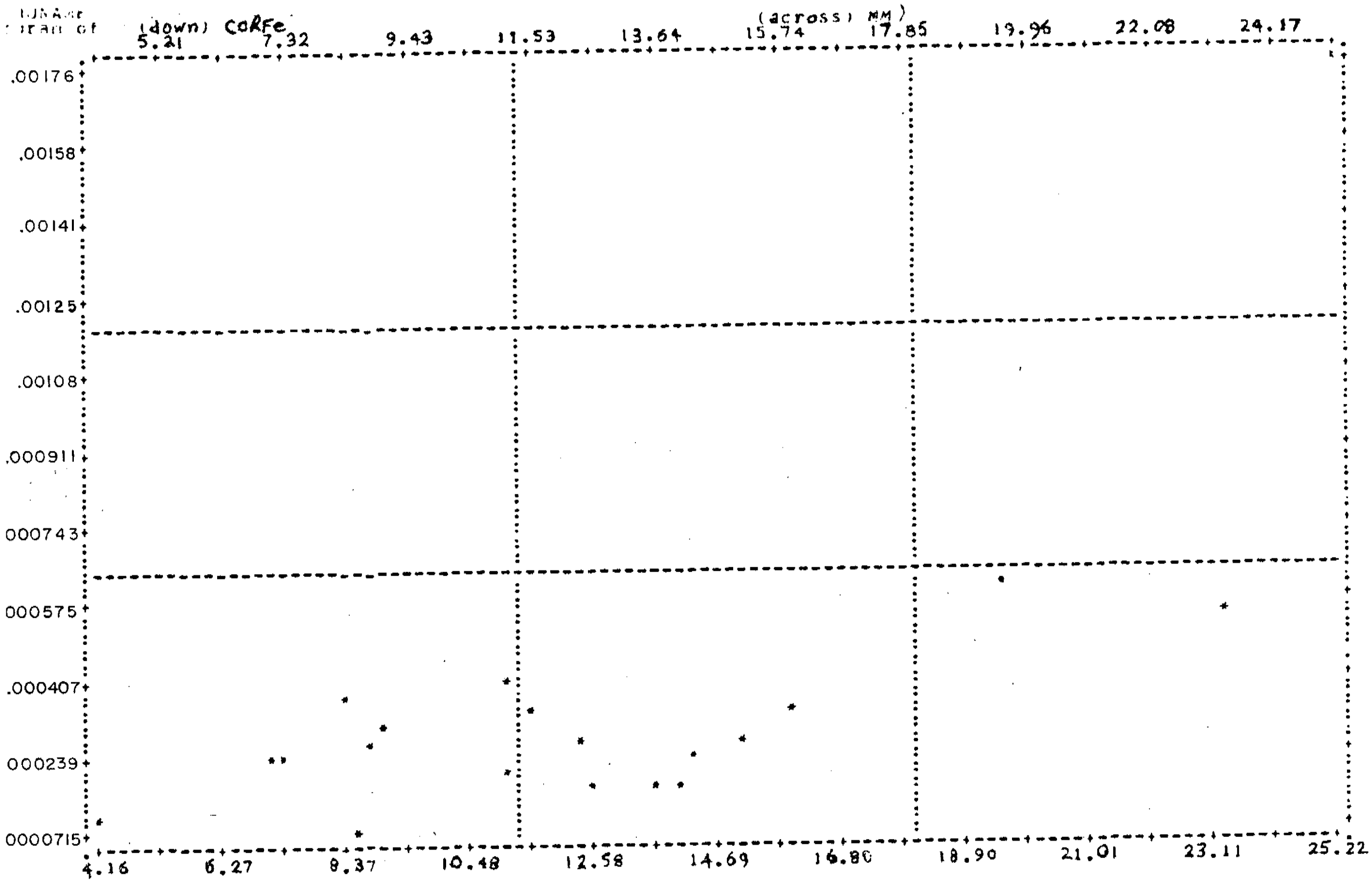
Appendix 10

SPSS Correlation Plots.

Abbreviations Used on Correlation Plots

Abbreviation	Meaning
TOTFE	total iron
FC	percent fixed carbon (dmmf)
KSAM	distribution coefficient, K , study samples
CEXFE	concentration of exchangeable iron within the non-pyritic inorganic mineral fraction
CCAFE	concentration of carbonate iron within the non-pyritic inorganic mineral fraction
COXFE	concentration of oxide iron within the non-pyritic inorganic mineral fraction
CORFE	concentration of organic iron within the hydrocarbon fraction
KG	distribution coefficient, K, Gluskoter et al.
MMG	percent mineral matter, Gluskoter et al.
FCG	percent fixed carbon (dmmf), Gluskoter et al.
PY	weight percent pyrite
MM	weight percent mineral matter

atch System

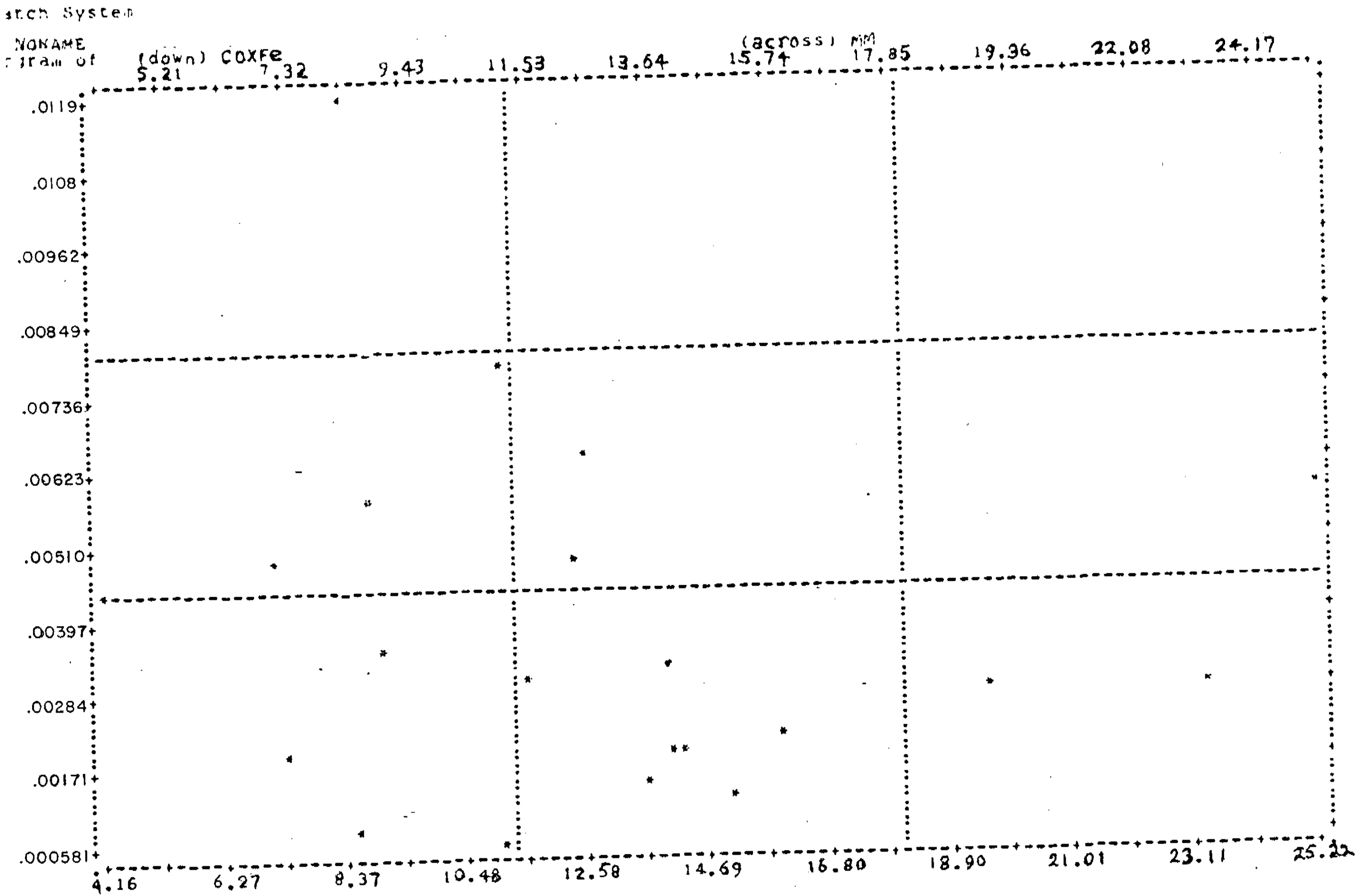


Concentration of organic iron within the hydrocarbon fraction of the coal compared to percent mineral matter

```
atch System

tics:
elation (R)-        0.70613      R squared      -       0.49862      Significance    -        0.00025
err of est  -       0.00026      Intercept (a)  -      -0.00024      Slope (b)       -        0.00005
ted values  -       20        -  Excluded values-       0            Missing values  -        0

          '*********' is printed if a coefficient cannot be computed.
```

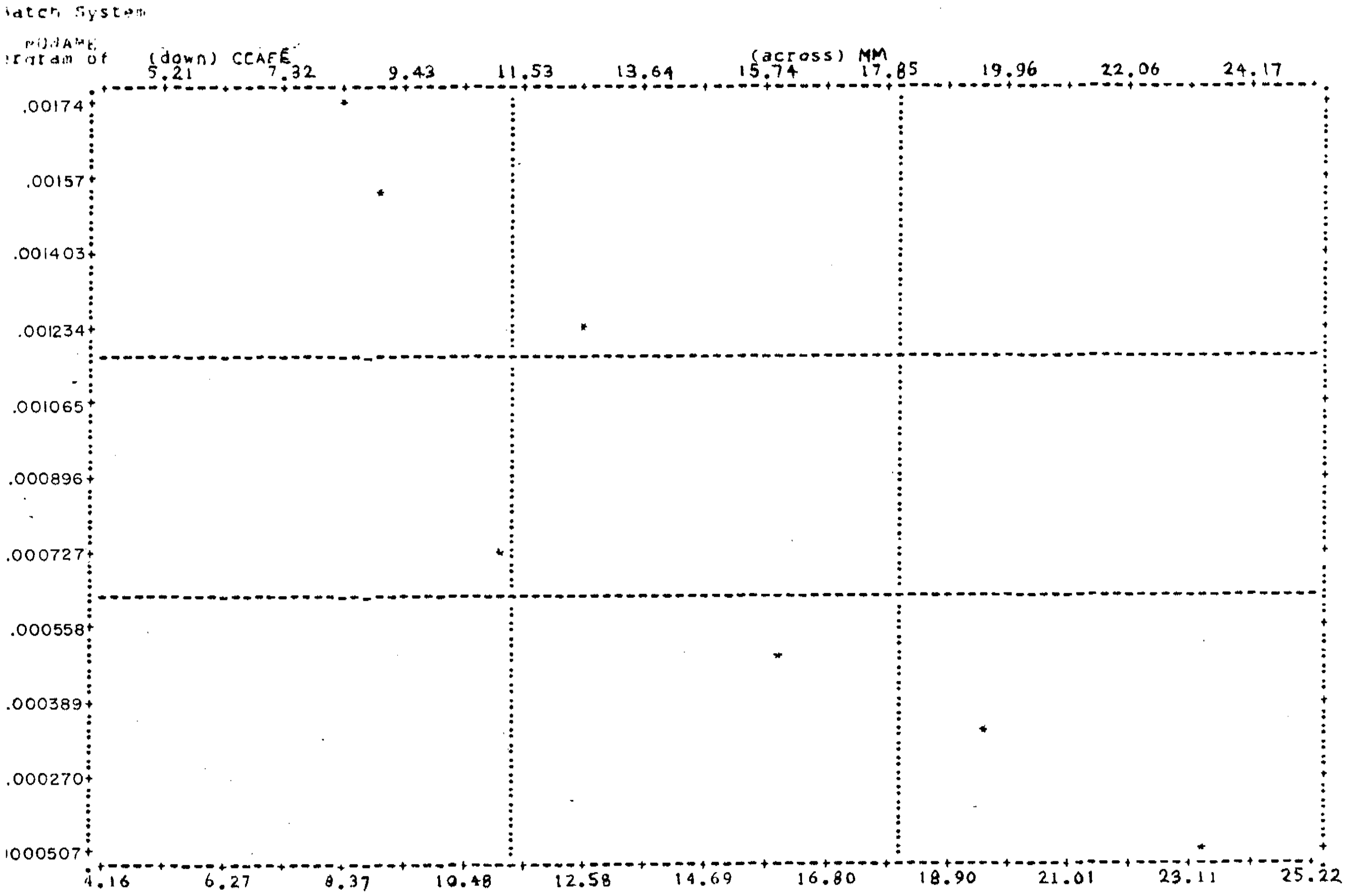


Concentration of oxide iron within the non-pyritic inorganic coal fraction compared to mineral matter

```
atch System

stics:
relation (R)-        -0.14321    R squared       -        0.02051    Significance    -        0.27348
 err of est -         0.00256    Intercept (a)   -        0.00466    Slope (b)       -       -0.00003
tted values -        20          Excluded values-         0          Missing values -         0

         '*********' is printed if a coefficient cannot be computed.
```

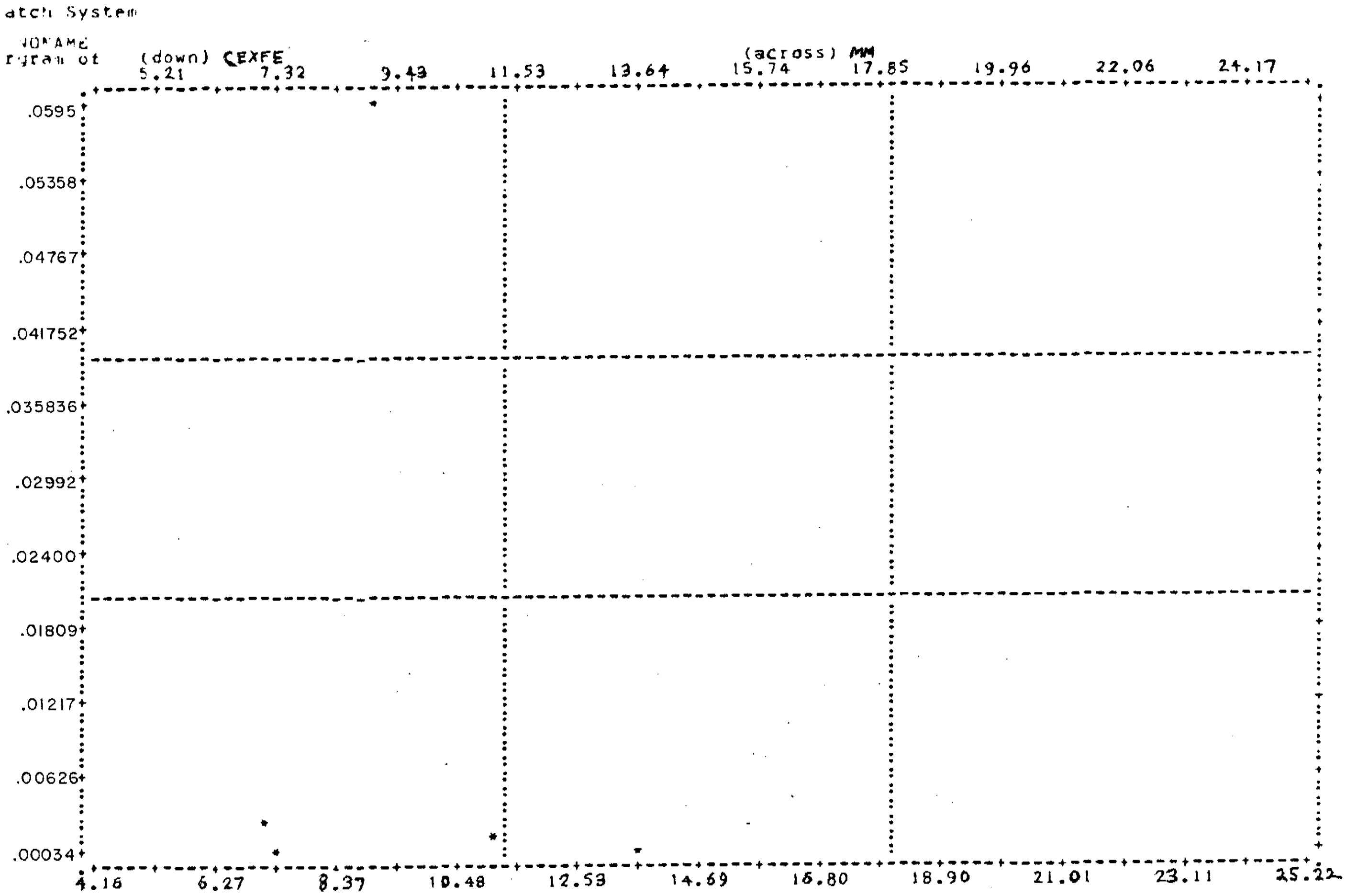


Concentration of carbonate iron within the non-pyritic inorganic coal fraction compared to mineral matter

```
atch System

tics:
elation (R)-     -0.91826     R squared      -     0.84321     Significance   -      0.00175
err of est -      0.00028     Intercept (a)  -     0.00239     Slope (b)      -     -0.00011
ted values -      7           Excluded values-     0           Missing values -      13

                  '*********' is printed if a coefficient cannot be computed.
```

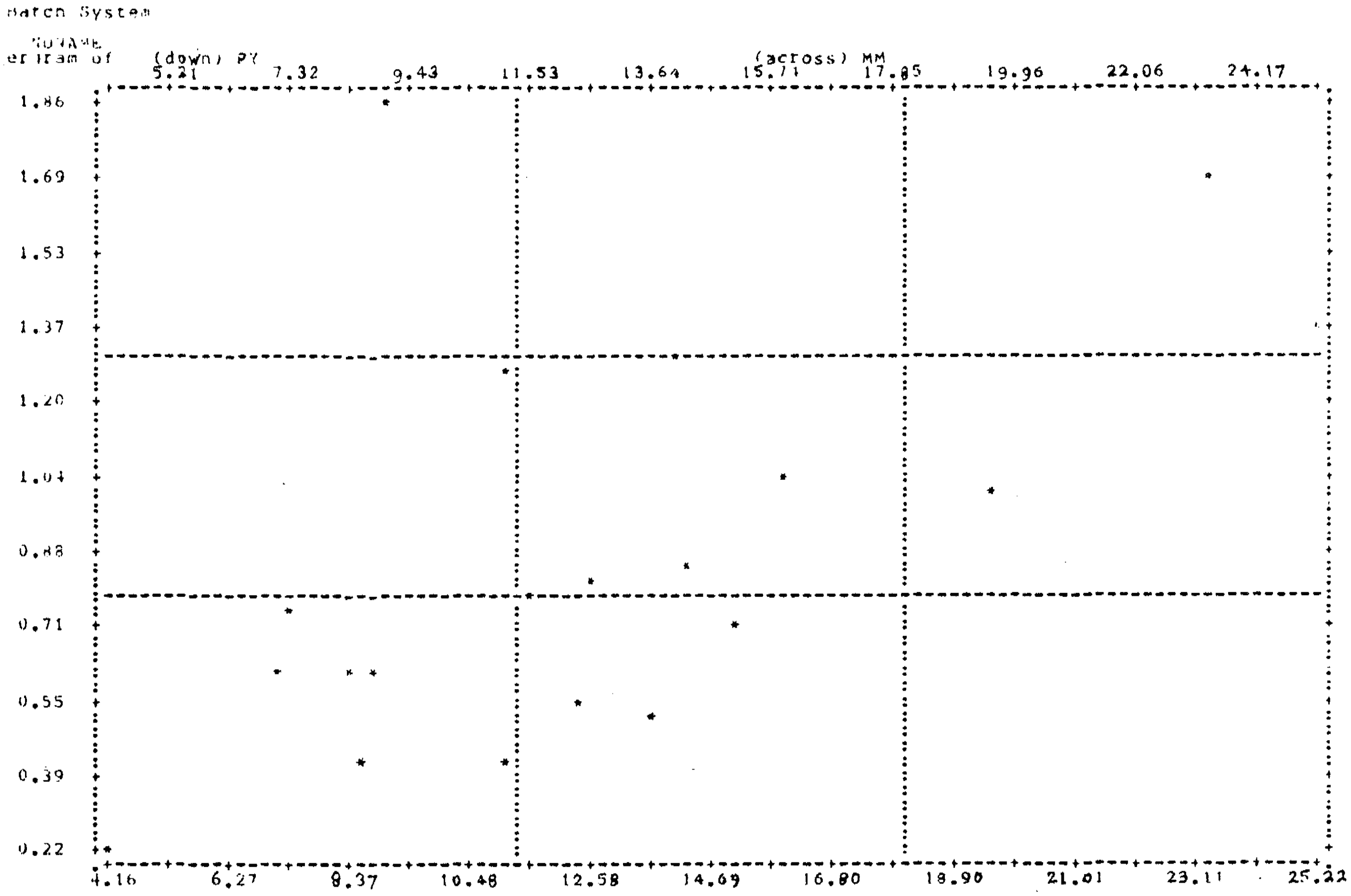


Concentration of exchangeable iron within the non-pyritic inorganic coal fraction compared to percent mineral matter

```
atch System

tics:
elation (R)-      -0.15513     R squared      -      0.02406     Significance   -     0.48164
err of est -       0.02964     Intercept (a)  -      0.02722     Slope (b)      -    -0.00116
ted values -       5           Excluded values-      0           Missing values -     15

             '*********' is printed if a coefficient cannot be computed.
```



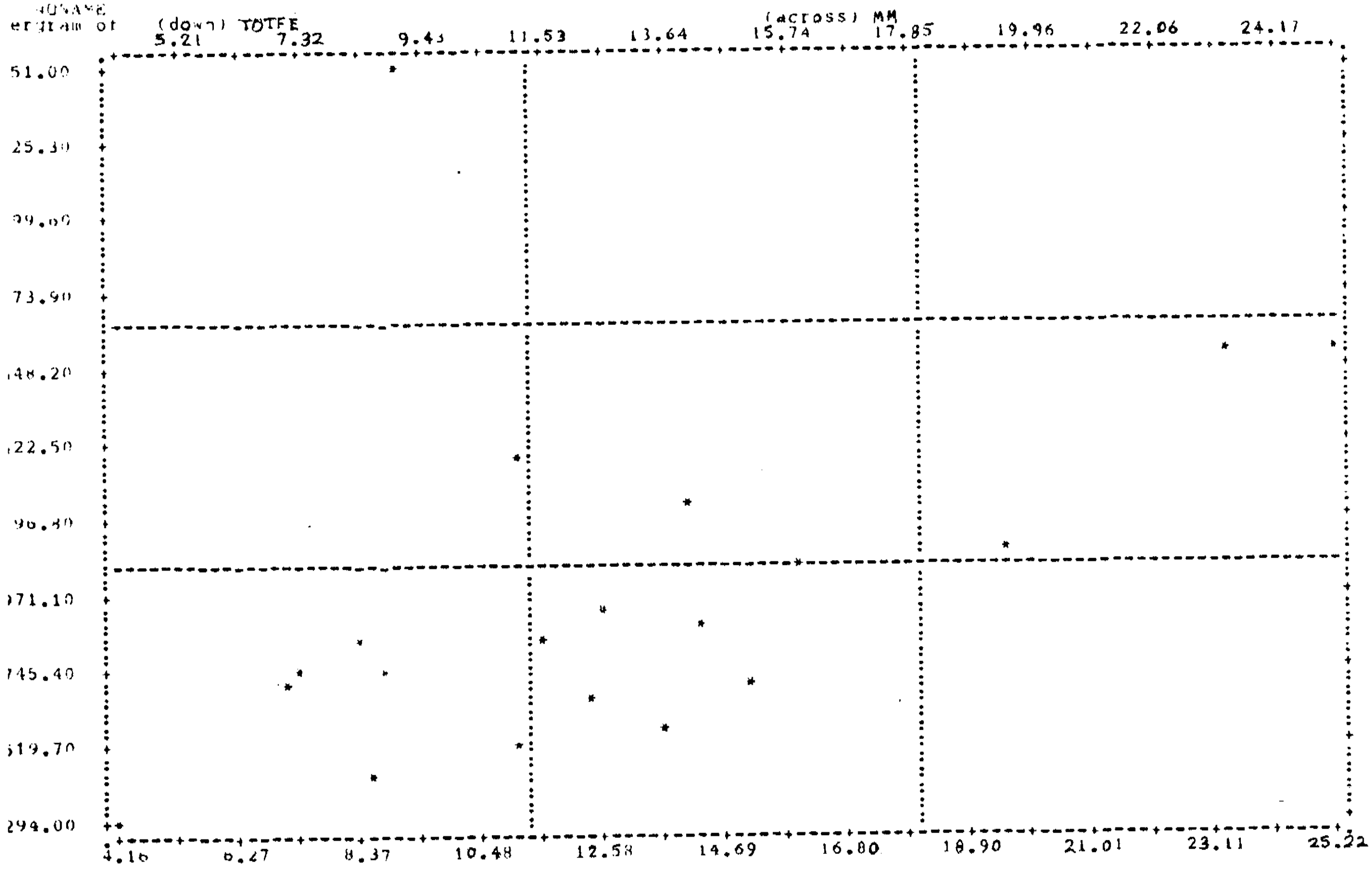
Percent pyrite compared to percent mineral matter

```
Batch System

stics:
relation (R)-       0.56247     R squared        -       0.31637      Significance   -        0.00542
 err of est -       0.36974     Intercept (a)    -       0.29006      Slope (b)      -        0.04529
tted values -       20          Excluded values-         0            Missing values -        0

              '********' is printed if a coefficient cannot be computed.
```

Batch System

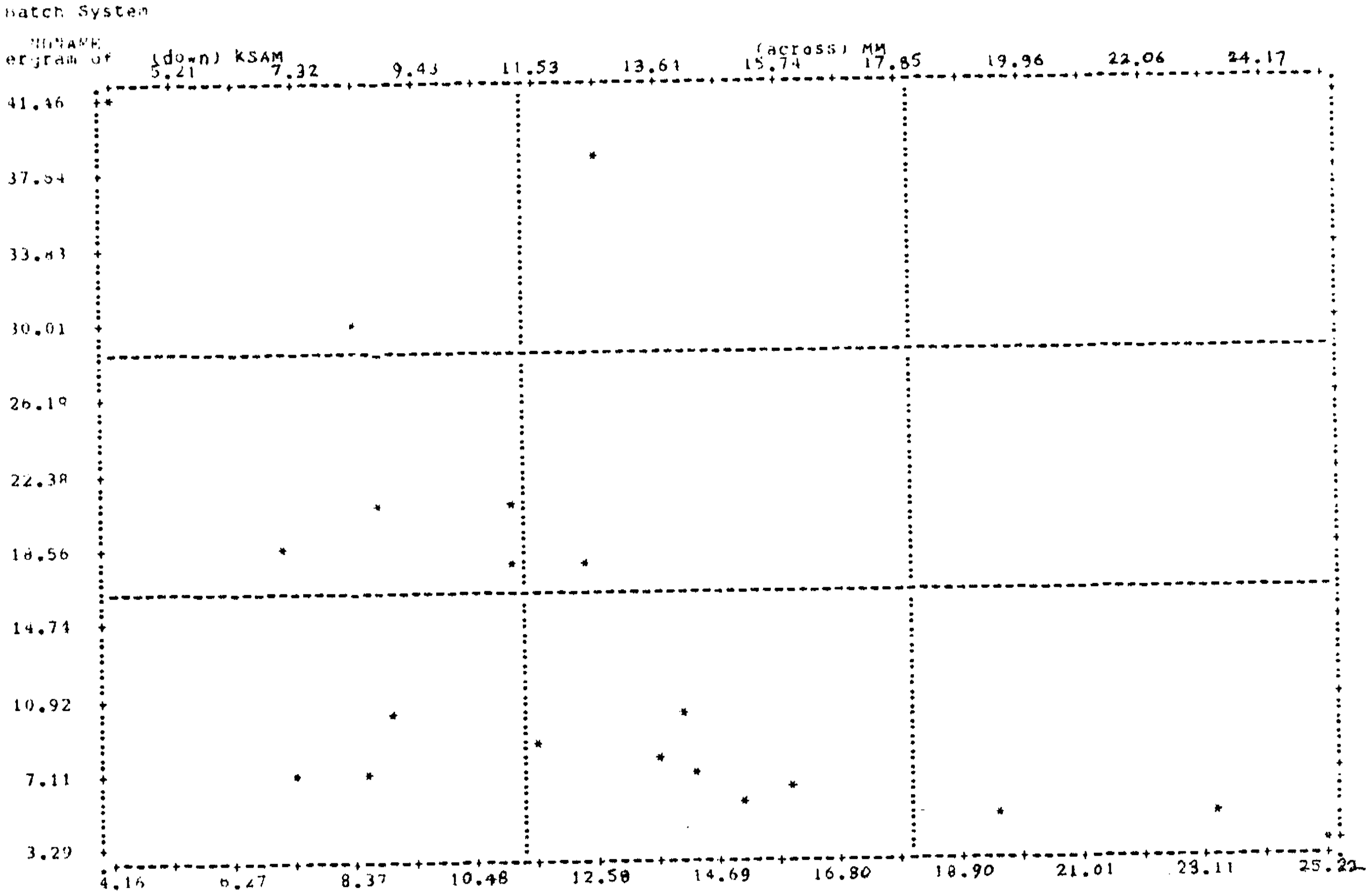


Total iron (ppm) compared to percent mineral matter

```
Batch System

istics:
rrelation (R)-      0.41349     R squared      -      0.19668     Significance   -      0.[illegible]
d err of est -   2031.63231     Intercept (a)  -   2031.06064     Slope (B)      -    237.57266
otted values -       20         Excluded values-        0         Missing values -      0

          '********' is printed if a coefficient cannot be computed.
```

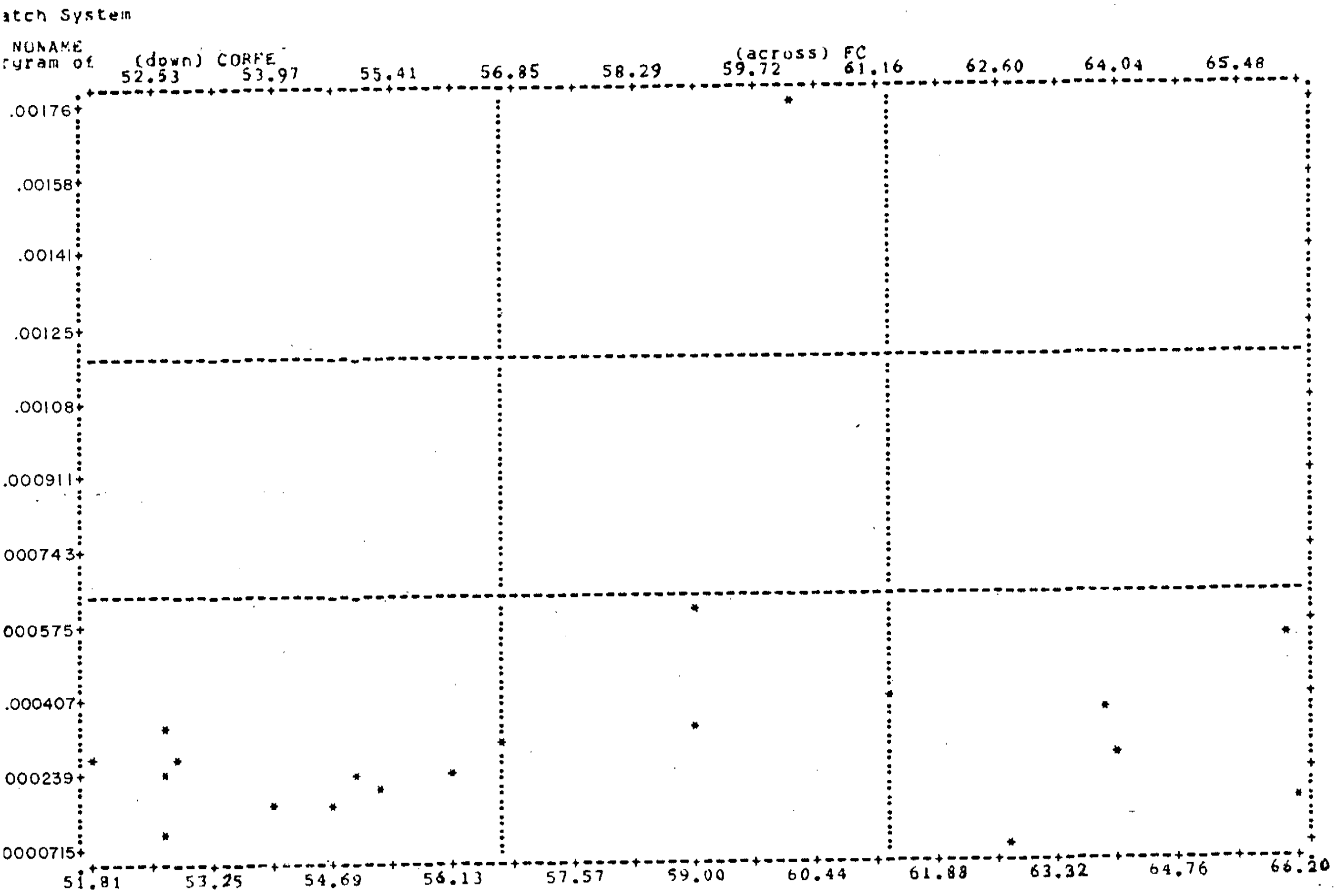


Distribution coefficient, K, compared to percent mineral matter

```
Batch System

istics:
rrelation (R)-      -0.58075     R squared      -     0.33728     Significance   -     0.00363
d err of est -       9.38017     Intercept (a)  -    29.98535     Slope (b)      -    -1.42060
otted values -      20           Excluded values-     0           Missing values -     0

          '********' is printed if a coefficient cannot be computed.
```

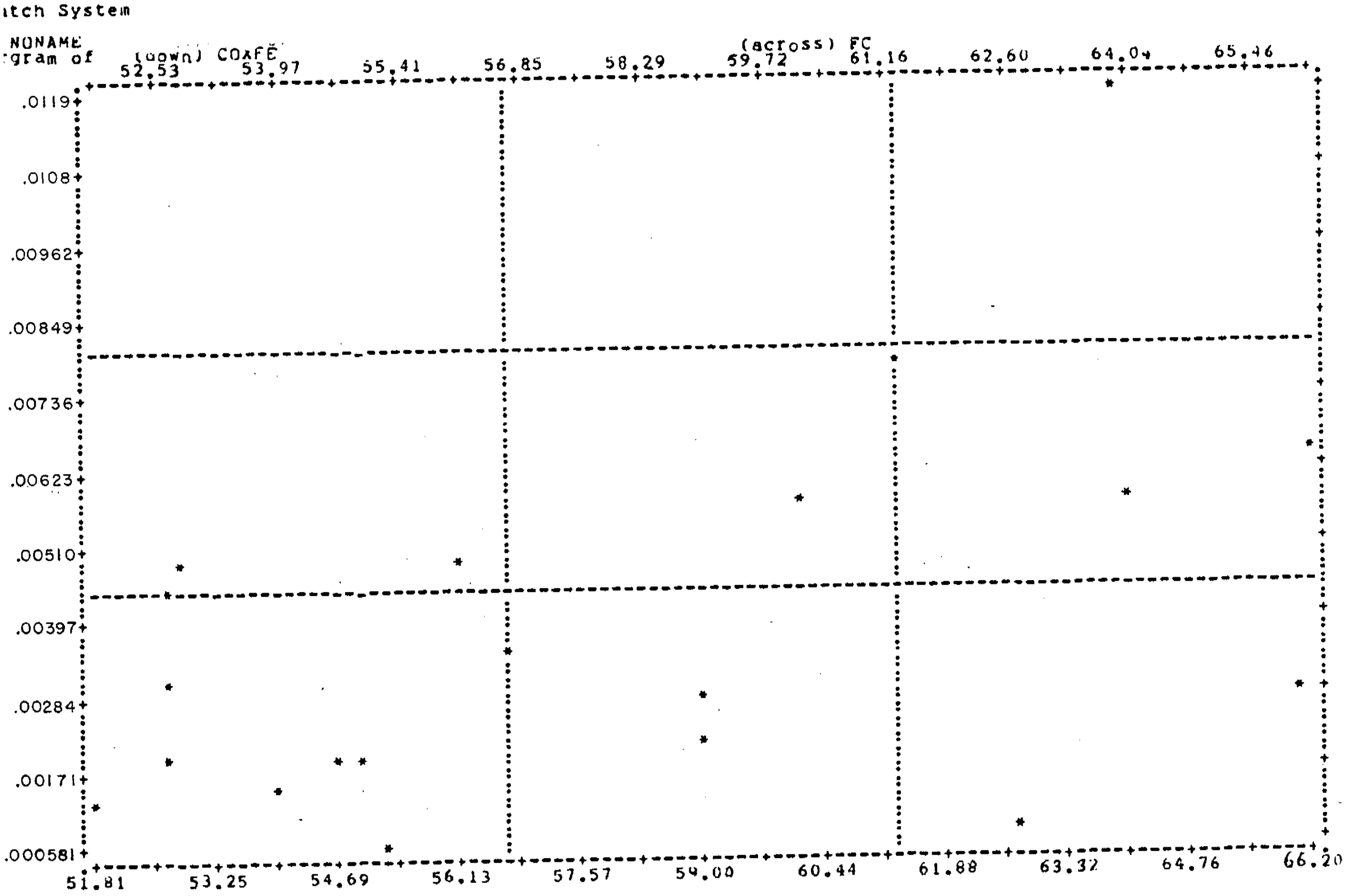


Concentration of organic iron within the hydrocarbon coal fraction compared to percent fixed carbon (dmmf)

```
atch System

tics:
elation (R)-        0.20951     R squared       -       0.04389     Significance   -        0.18767
err of est -        0.00035     Intercept (a)   -      -0.00053     Slope (b)      -        0.00002
ted values -       20           Excluded values-        0           Missing values -        0

            '*********' is printed if a coefficient cannot be computed.
```

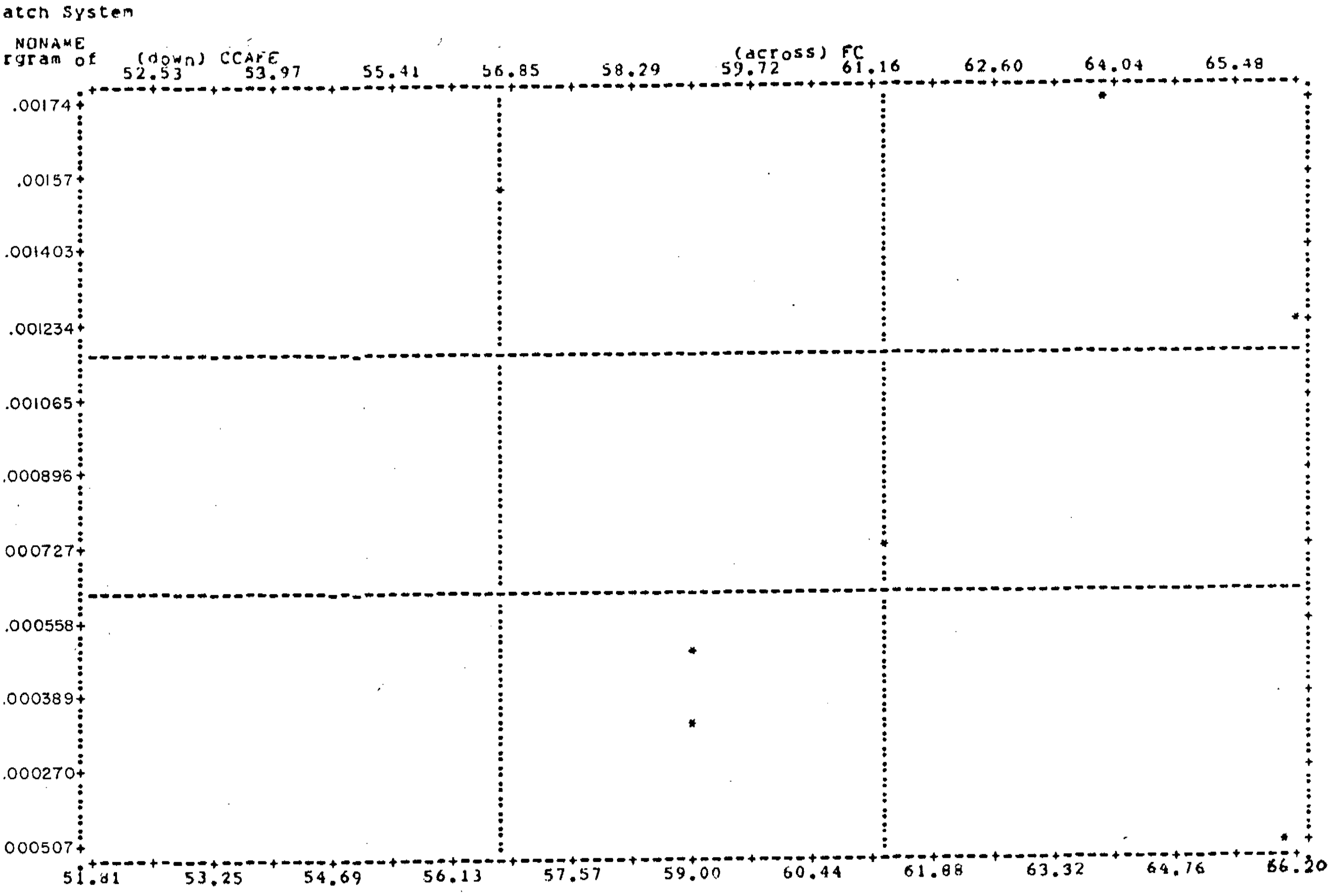


Concentration of oxide iron within the non-pyritic coal fraction compared to percent fixed carbon (dmmf)

```
atch System

tics:
elation (R)-       0.47929     R squared      -      0.22972    Significance   -       0.01625
err of est -       0.00254     Intercept (a)  -     -0.01250    Slope (b)      -       0.00028
ted values -      20           Excluded values-      0          Missing values -       0

          '*********' is printed if a coefficient cannot be computed.
```



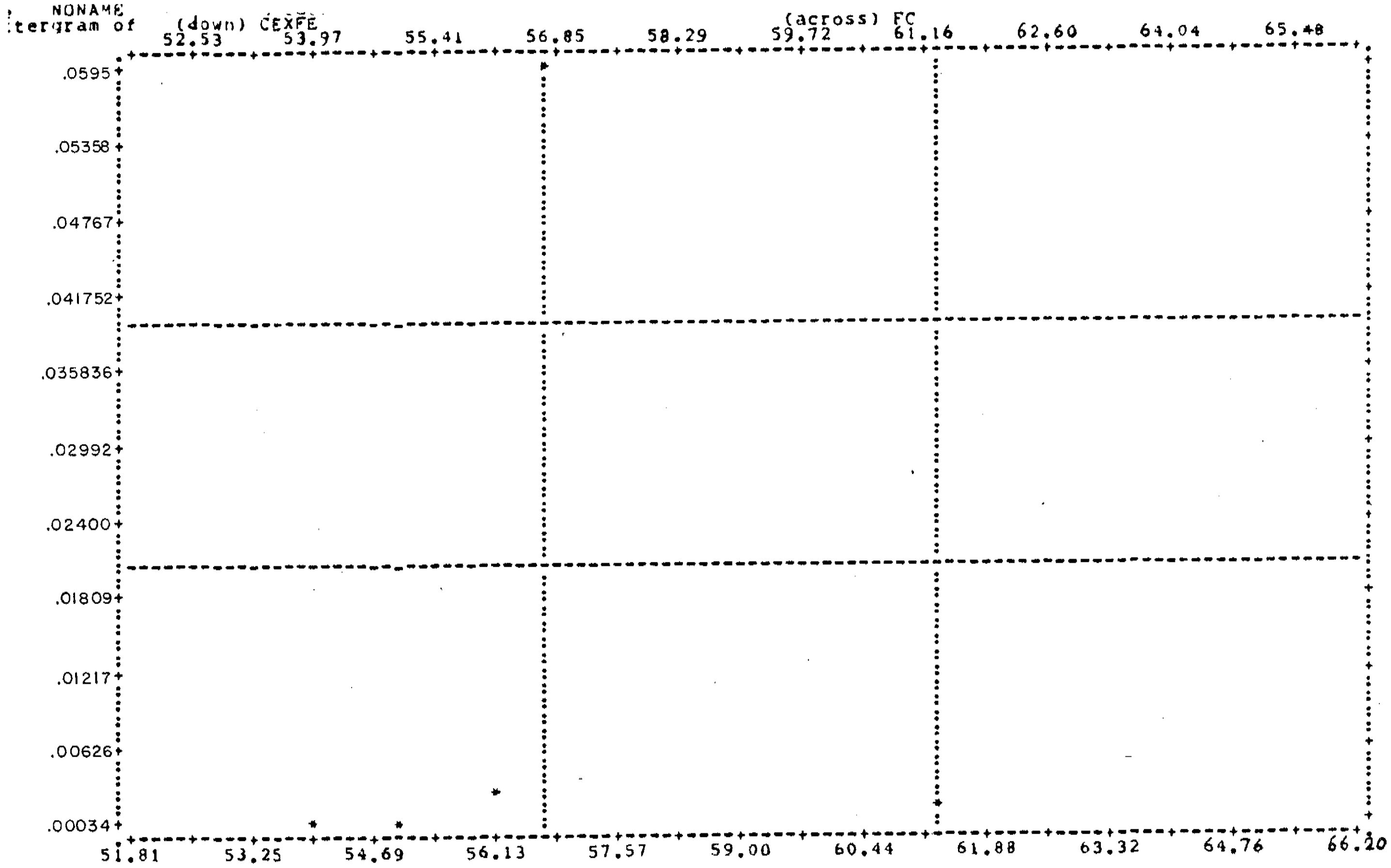
Concentration of carbonate iron within the non-pyritic coal fraction compared to percent fixed carbon (dmmf)

```
atch System

tics:
elation (R)-        -0.05338      R squared      -        0.00285        Significance   -          0.45475
err of est -         0.00071      Intercept (a)  -        0.00145        Slore (b)      -     -0.926670-05
ted values -         7            Excluded values-        0              Missing values -          13

                   '*********' is printed if a coefficient cannot be computed.
```

; Batch System

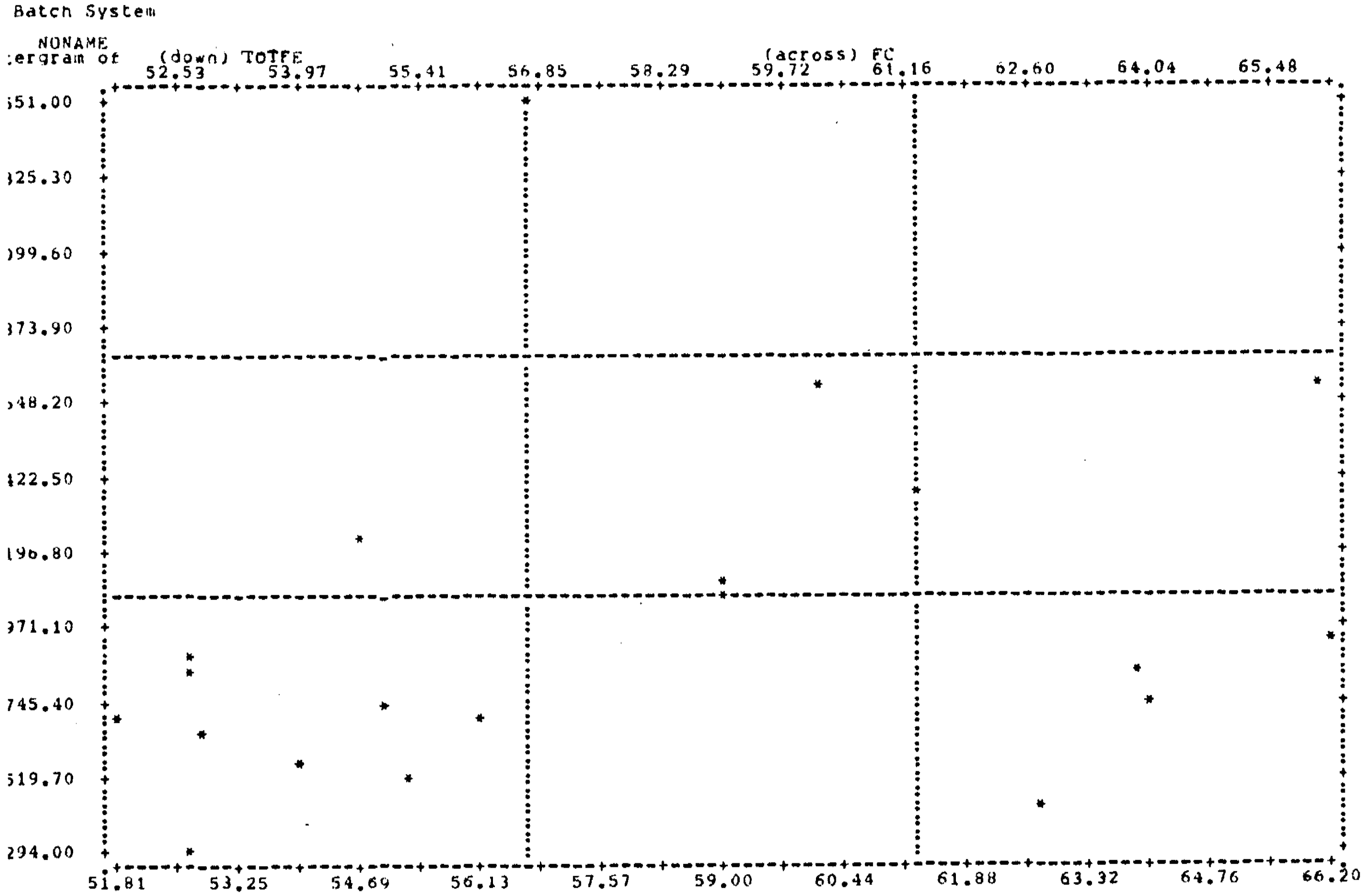


Concentration of exchangeable iron within the non-pyritic coal fraction compared to percent fixed carbon (dmmf)

```
; Batch System

.istics:
'rrelation (R)-       0.04028     R squared       -      0.00162     Significance    -        0.47436
:d err of est  -      0.02998     Intercept (a)   -     -0.00820     Slope (b)       -        0.00038
.otted values  -      5           Excluded values-       0           Missing values  -        15

                '*********' is printed if a coefficient cannot be computed.
```



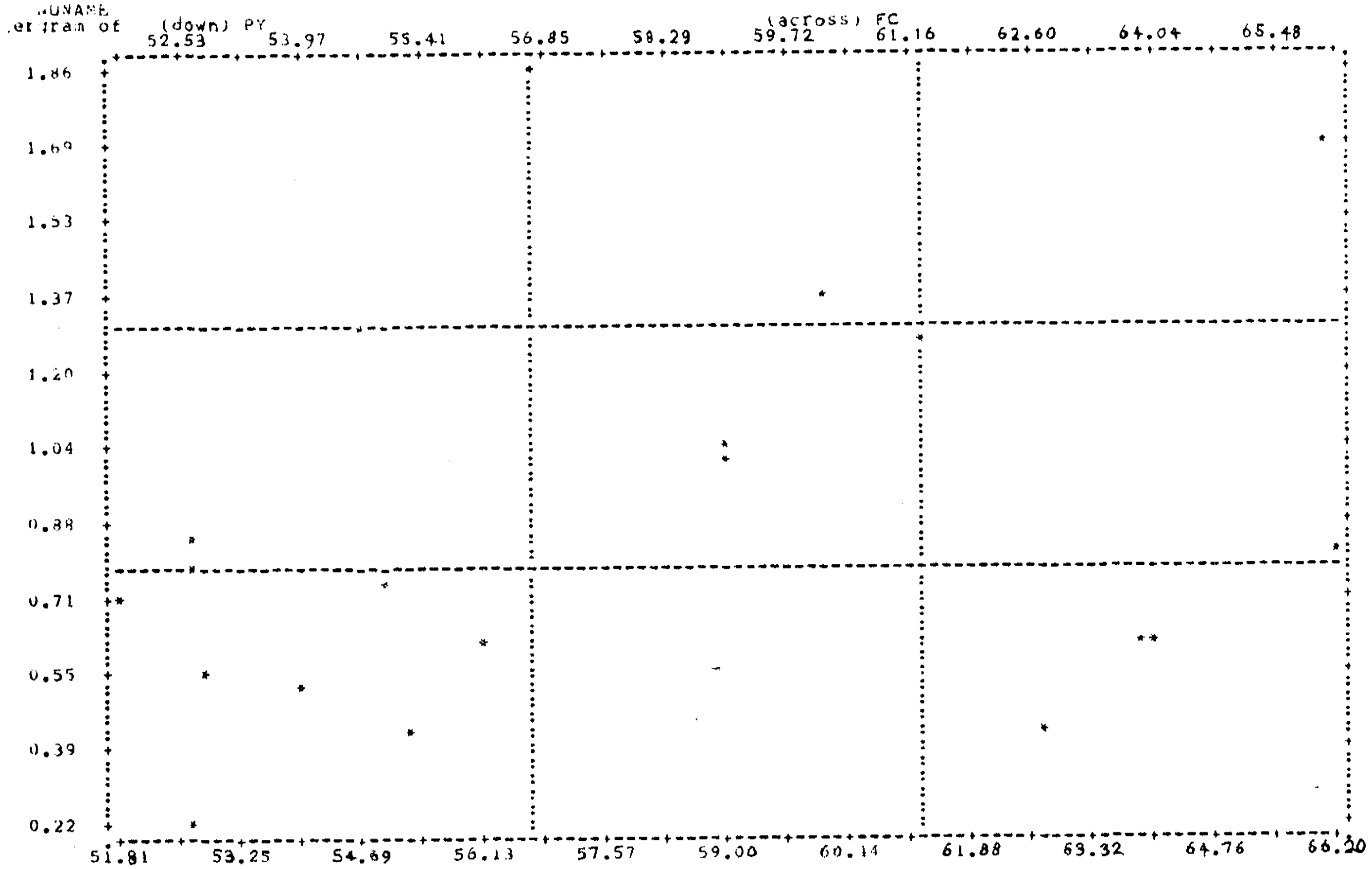
Total iron (ppm) compared to percent fixed carbon (dmmf)

```
 Batch System

istics:
rrelation (R)-      0.27166     R squared      -      0.07380     Significance   -      0.12330
d err of est -   2825.74345     Intercept (a)  -  -4278.23067     Slope (b)      -    161.07505
otted values -     20           Excluded values-      0           Missing values -      0

              '********' is printed if a coefficient cannot be computed.
```

Batch System

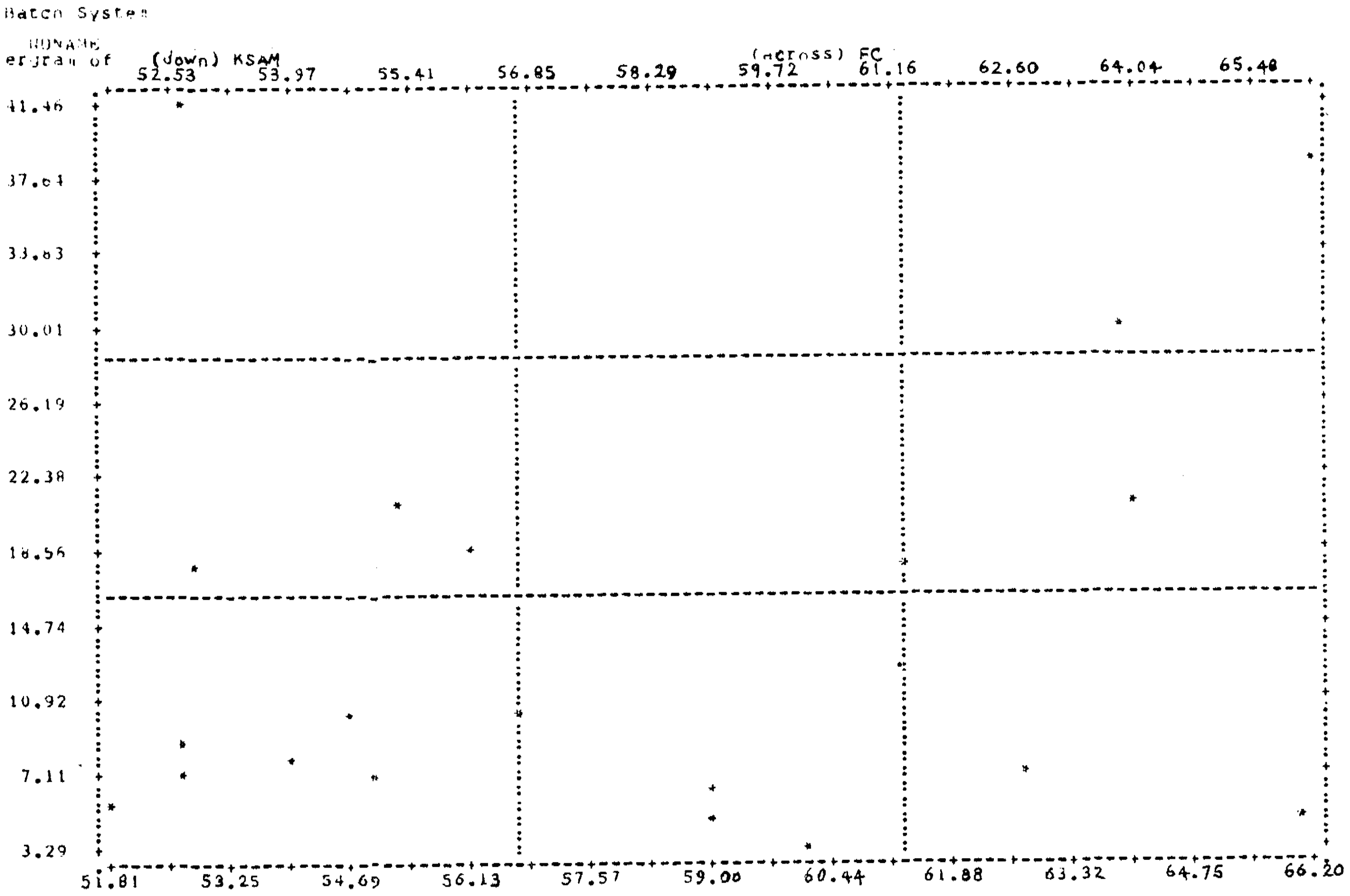


Percent pyrite compared to per-
cent fixed carbon (dmmf)

```
 Batch System

istics:
rrelation (R)-        0.28657     R squared        -       0.08212      Significance    -        0.11629
d err of est -        0.42643     Intercept (a)    -      -0.62579      Slope (b)       -        0.02568
otted values -       20           Excluded values-         0            Missing values  -        0

              '********' is printed if a coefficient cannot be computed.
```

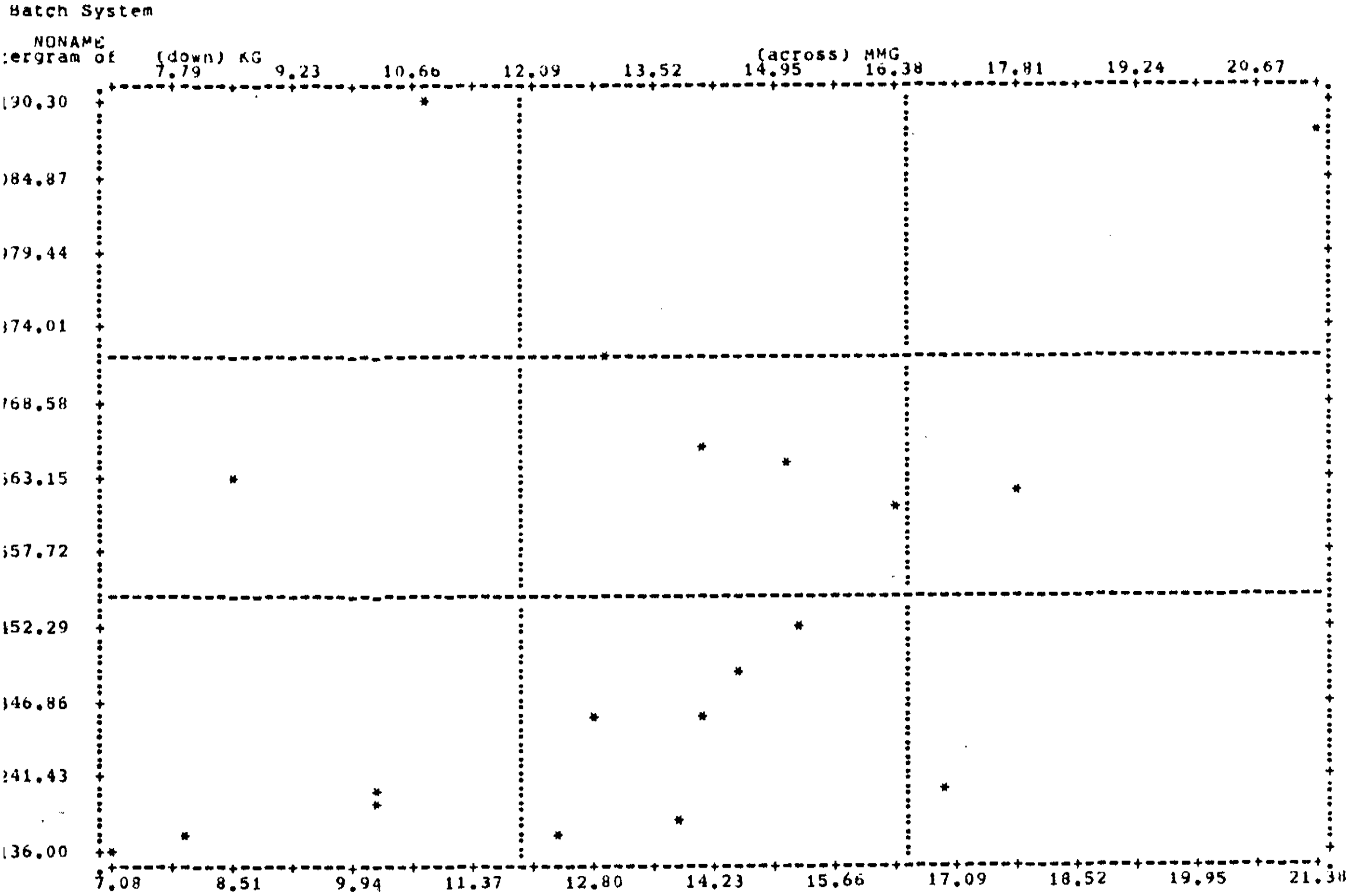


Distribution coefficient, K, compared to percent fixed carbon (dmmf)

```
Batch System

stics:
relation (R)-      0.18519     R squared       -      0.03430     Significance   -       0.21780
 err of est -      11.32312    Intercept (a)   -    -10.40396     Slope (b)      -       0.43091
tted values -      20          Excluded values-       0           Missing values -       0

          '*********' is printed if a coefficient cannot be computed.
```



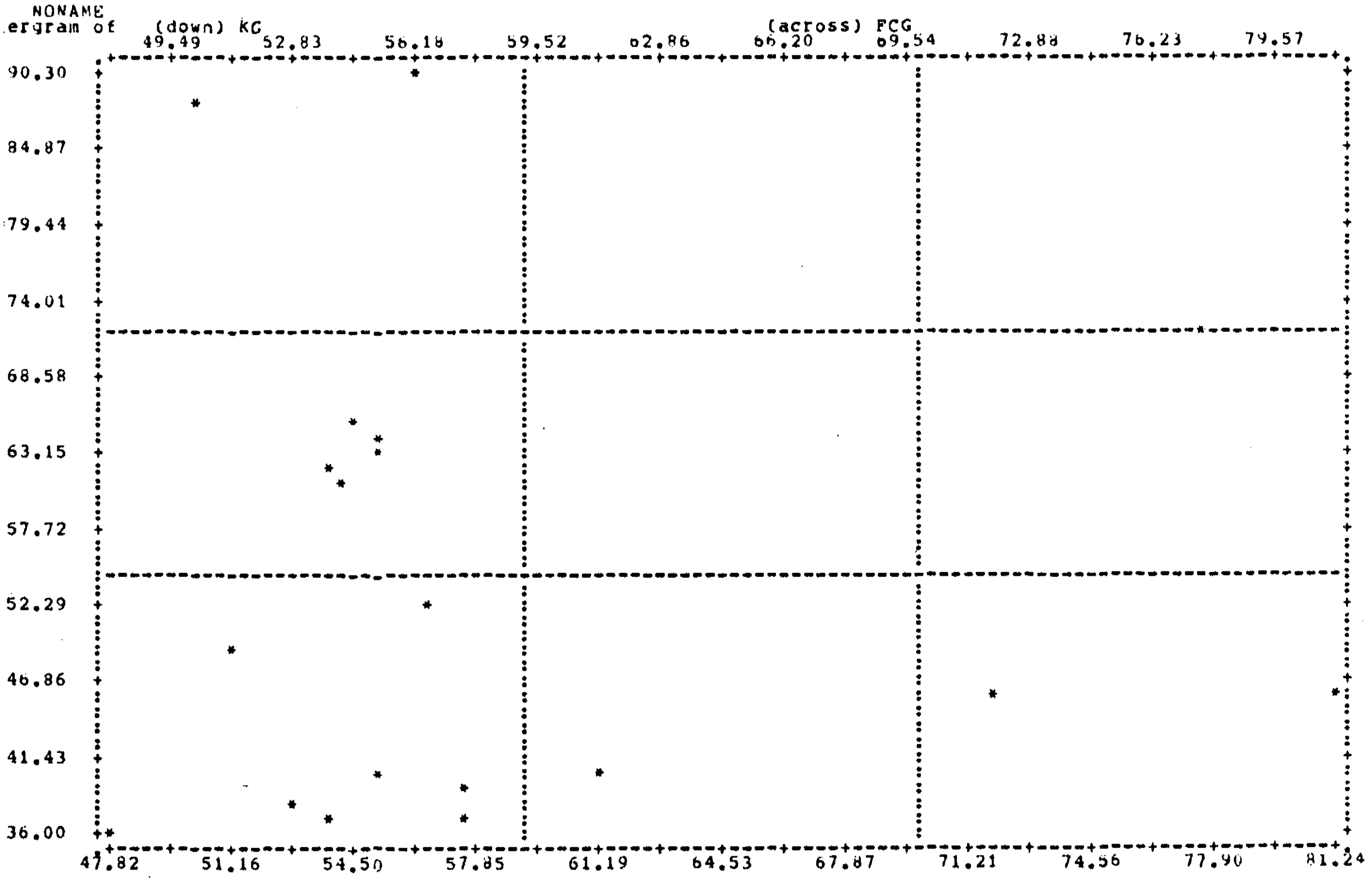
Distribution coefficient, K for Gluskoter et al. data compared to percent fixed carbon (dmmf)

```
Batch System

stics:
relation (R)-       0.41880     R squared      -        0.17539     Significance    -       0.03716
 err of est -     305.76000     Intercept (a)  -      -20.15241     Slope (b)       -      38.01473
tted values -        19         Excluded values-        0           Missing values  -       1

            '********' is printed if a coefficient cannot be computed.
```

```
Batch System
```



Distribution coefficient, K, for Gluskoter et al.
data compared to percent mineral matter

```
Batch System

stics:
relation (R)-      -0.02736     R squared      -       0.00075     Significance   -      0.45574
 err of est -     336.58458     Intercept (a)  -     542.63151     Slope (b)      -     -0.99843
tted values -       19          Excluded values-       0           Missing values -      1

           '*********' is printed if a coefficient cannot be computed.
```