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A STUDY OF THE FIRST ROW TRANSITION ELEMENTS AS A GROUP IN A SECTION OF THE NEW ALBANY SHALE (DEVONIAN-MISSISSIPPIAN) OF SOUTHERN INDIANA

By

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ABSTRACT

A STUDY OF THE FIRST ROW TRANSITION ELEMENTS AS A GROUP IN A SECTION OF THE NEW ALBANY SHALE (DEVONIAN-MISSISSIPPIAN) OF SOUTHERN INDIANA

By

Marcia Kay Schulmeister

The use of first row transitions elements (FRTE) as a group has been proposed as a new tool for interpretation of paleochemical environments (Wilson et al., 1988; Piotrowski, 1991). This study evaluates the use of FRTE in interpretating paleoredox conditions assigned to sediements in three Members of the Devonian New Albany Shale. FTRE distribution among redox sensitive mineral phases within the shale is predicted based on Goldschmidt's rules and crystal field theory. Metal partitioning among untreated shale, nonreactive shale materials and 5 chemically separable phases is determined, through the use of selective chemical extractions. Resulting metal distributions do not support the predictions regarding FRTE distribution as a function of redox condition. Metal distributions is unique for each shale component considered, and certain components are more important than others in controlling the overall trace metal signatures in the shale. The findings indicate that certain components of the shale may be useful as indicators of ancient chemical environments.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

The distribution of trace elements in geologic materials can provide insight regarding the chemistry of past sedimentary environments. For this reason, groups of elements with predictable chemical behaviors have been recognized, and their relative abundances in geologic materials evaluated. Rare earth elements, for example, because of their ionic size and relatively constant charge have been used to predict sediment provenance in shales (Andre et al., 1986). First transition series elements have been proposed as new tool for interpreting ancient geochemical conditions (Piotrowski, 1991; Piotrowski et al., 1989; Wilson et al., 1988; Allegre and Michard, 1973). Differing coordination chemistries and multiple valance states among the first row transition elements (FRTE) allow each element a unique response to variations in chemical environments. Thus, as a group FTRE may be more sensitive paleochemical indicators than other groups of elements (Piotrowski, 1991). In this study, the sensitivity of FRTE as recorders of paleogeochemical environments is evaluated in an examination of a marine shale which is thought to have been deposited during a transition from oxic to anoxic marine bottom water conditions.

First row transition elements in shales

First row transition elements are among the most abundant trace elements in sedimentary systems (Turekian and Wedepohl, 1961) and are thought to be incorporated into marine sediments more readily than other trace elements (Taylor and McClennan, 1985). A marine black shale was chosen for this study because black shale sediments typically sequester higher concentrations of trace elements than do other materials (Jacobs et al., 1985, 1987; Manheim, 1981; Vine and Tourtelot, 1970; Brewer and Spencer, 1974, Calvert and Price; 1970, 1983). In addition, because black shale consists of a number of mineral phases, the distribution of trace elements among chemically separable fractions offers accessible information about the environment in which the shale formed.

Marine shales are composed of two mineralogic fractions: a detrital fraction which consists of the weathering products of nearby terrestrial sources (Shaw et al, 1990; Piotrowski; 1991, Wedepohl, 1968), and a hydromorphic fraction, composed of authigenic mineral phases and organic materials derived from the water column. The mineralogy of the detrital fraction (made up primarily of silt and clay) may provide information about sediment provenance. The hydromorphic fraction, however, forms in response to the chemical environment of deposition and thus may yield information about the chemistry of the depositional setting. The hydromorphic fraction includes carbonate, Mn- and Fe-oxide, and sulfide minerals, in addition to organic materials (Berner, 1980). Metals sorped on to clay surfaces may also be a part of the hydromorphic phase.

The affinity of trace elements for each of the hydromorphic phases results from a complex interplay of thermodynamic and kinetic controls acting during deposition and diagenesis (Emerson et al., 1983; Jacobs et al., 1985). Ions are incorporated into and released from a phase during adsorption, desorption, coprecipitation, precipitation and dissolution reactions (Gibbs, 1973). Environmental conditions such as pH, pe, organic productivity and amount of SO_4 present in a system will effect the rates and extent of trace element distribution. In most adsorption or precipitation reactions, it is a combination of these factors which determines the overall free energy change which occurs during ionic transfer, and controls trace element partitioning among phases (Dawson et al., 1985).

Although the above mentioned environmental controls make prediction of trace metal distributions in sediments difficult, atomic structural controls on FRTE distribution provide a means of approximating the incorporation of FRTE into some mineral phases. Crystal field stabilization energies (CFSE), lattice energies and ionic potential have been used to explain the ultimate preference of one element over another during its incorporation into a particular ordered mineral phase (Burns, 1970, McKenzie, 1975). The use of CFSE in predicting trace element distributions is discussed in Appendix A, and is used in this report to predict the distribution of the FRTE as a result of changes in sedimentary redox conditions.

First row transition element partitioning in a Devonian black shale

Piotrowski (1991) first demonstrated that FRTE distribution in a black shale may provide information regarding the shale's depositional origin. In a study of the Antrim Shale (Devonian) of Michigan, Piotrowski (1991) measured the distribution of FRTE in detrital and hydromorphic fractions of the shale in samples collected from three lithologically distinct Antrim Shale horizons. Several samples were collected within each horizon from quarry walls approximately 300 meters apart. A similar FRTE distribution within lithologic strata was noted for untreated shale, three hydromorphic phases, and sediment remaining after all hydromorphic phases were removed (residual material). This result indicates that either uniform chemical/sedimentary conditions may have existed during the deposition of each horizon and that the associated trace metal signature has survived possible alteration due to burial diagenisis, or that it was altered uniformly by late diagenetic overprinting.

Further results of Piotrowski (1991) demonstrate that the distribution of individual FRTE among hydromorphic phases of the shale are distinctly different from each other, and that certain phases contribute more metals to total shale composition than do others. This finding indicates that isolation and analysis of chemically separable hydromorphic phases provides more detailed information about the shale's ultimate origin, than does analysis of the untreated (bulk) shale exclusively. The FRTE signature in a hydromorphic phase may be directly related to the phase's response to environmental conditions (Piotrowki, 1991).

A comparison of FRTE distributions by Piotrowski (1991) in the three lithologically distinct horizons shows FRTE partitioned differently within each unit. The differences suggests that chemical and/or sedimentary conditions, which occurred during formation of the shale, may have been unique for each environment. Trace metal abundances in these fractions might thus be used to determine original environmental conditions if the controls on the trace metal distributions are understood. Factors which determine the distributions of the FRTE in various phases of the shales were not discussed by Piotrowski (1991) and are the subject of this study.

The scope of this project

Because elements with multiple valance states are sensitive to oxidation-reduction conditions, their distribution among redox-sensitive mineral species should vary in accordance with variable redox environments. Sediment associated with variable redox conditions may therefore contain trace-metal signatures which correlate with such changes (Finney and Mitchell, 1988; Jacobs et al., 1985). First row transition elements are the most electronegative of the transition elements, are the strongest oxidizing agents among the transition series and are quite sensitive to redox changes. For this reason, they are an excellent chemical group for study in redox systems. The most common valance states for the FRTE are Sc^{+3}, Ti^{+4}, $V^{+3},^{+4}$, $Cr^{+3},^{+6}$, $Mn^{+2},^{+3}$, $Fe^{+2},^{+3}$, $Co^{+2},^{+3}$, Ni^{+2}, $Cu^{+1},^{+2}$ and Zn^{+2} (Brookins, 1988). Under normal marine conditions, FRTE are oxidized in the water column, and associate with minerals formed in oxidizing conditions. Elements that are more energetically favored than others will partition more readily into the oxide phase. Enrichment of certain FRTE in the oxide phase should result in subsequent depletion of those elements in the other mineral phases forming in the same environment. It is the goal of this project to describe the correlation between FRTE distributions in individual components of a black shale and proposed sedimentary redox assigned to the same samples.

Predicted first row transition element distributions

The FRTE distribution in untreated (bulk) shale samples is a thought to be a cumulative expression of the metals contained in detrital and hydromorphic components of the shale. Different FRTE abundances among untreated shale samples may indicate differences in detrital material contents, original depositional environments or post depositional events associated with individual samples. For this reason, it is difficult to discern the effects of redox on FRTE patterns using the bulk shale fraction exclusively. Specific controls on the distribution of the elements are therefore explored through isolation and study of separable (hydromorphic) components of the shale.

Because the residual fraction is thought to contain detrital materials, it may be used to evaluate variability in the sediment provenance. Using Goldschmidt's geochemical classification of the elements (1954), predictions about FRTE distribution in the residual fraction are made on the basis of geochemical affinities of FRTE. Scandium, Ti, V, Cr, Mn and Fe are classified by this scheme as lithophile elements and are typically found in silicates. Cobalt and Ni are often observed to accompany Fe during incorporation of fe in the mineral phase, and Cu, Zn (and Fe) readily form sulfides as chalcophile elements. Lithophilic elements (Ti, V, Fe, Mn) are often used to distinguish detrital from authigenic components in sedimentary rocks (Shaw et al., 1990), while chalcophile-siderophile elements (Ni, Cu, Ni, Fe, Co-Zn) are more common in the authigenic mineral phases. (Piotrowski, 1991; Shaw et al., 1990). Based on these observations, the concentrations of FRTE in the residual fraction are expected to decrease with increase in atomic number, reflecting the decreasing lithophilic character across the group.

In addition to detrital sediments, high molecular weight organic materials, which are enriched in metals, are likely to be contained in the residual fraction. These materials result from chlorophyll and heme pigments of living matter which undergo burial diagenesis, and are diagenetically altered to form tetrapyrrole complexes (Orr et al., 1958; Lewan, 1970). The complexes are insoluble in the strongest of acids, and are inert to metal exchange reactions (Caughey and Corwin, 1955). Crystal field theory can be used to predict which of the FRTE will be found in the tetrapyrrole sites (Lewan and Maynard, 1982). Based on their availability in reducing conditions as bivalent cations, and because they have the highest CFSE in the octahedral and square planar tetrapyrrole binding sites, V and Ni are the most likely FRTE to be found in insoluble organic materials (Maynard, 1982; Vine and Tourtelot, 1970).

First row transition element distributions in the hydromorphic fractions are more likely to provide information about redox conditions than are distributions in the residual fraction, because hydromorphic phases result from changes in the chemical environment. As in organic material, FRTE distributions in oxide minerals may also be predicted using crystal field theory. A gain in CFSE results from replacing Mn^{+4} with Co^{+3}, and Mn^{+2} and Fe^{+3} with Co^{+3} in Mn-oxides (McKenzie, 1975; Dawson et al.,1985). McKenzie (1975) demonstrates that only low spin Co^{+3} has a higher CFSE than Mn^{+3} for trivalent oxides of Mn, but that Cu^{+2}, Ni^{+2}, and Co^{+2} may replace Mn in hausmanite (Mn_3O_4), a mineral which contains tri- and divalent Mn. Because the Fe-oxide ligand binding site is similar to that of Mn-oxide, the same principles may be applied to the Fe-oxide phase. Thus Ni, Cu and Co should be fractionated among the oxides in sediments associated with oxidizing conditions and a corresponding lack of Ni, Cu, and Co should be apparent in the other mineral phases.

The comparison of FRTE distribution and redox environments is made in this study using a geologic section which is believed to have been deposited during a period od shifting paleoredox conditions. The Devonian-Mississippian, New Albany Shale of Indiana was chosen for study because it is thought to have been deposited during a period of shifting marine bottom water redox conditions. FRTE abundances in samples spaning the change in redox conditions are plotted, and the correlation between pattern shapes and redox environments is examined.

THE NEW ALBANY SHALE AND EARLY DIAGENETIC REDOX CONDITIONS

Depositional environment

The New Albany Shale was deposited in the Illinois Basin from Late Givetian to Early Kinderhookian. The formation attains a thickness of 50 feet in the southern Indiana study area, and dips southwestward, toward the basin's center in southeastern Illinois. Core samples collected for this study are from a "deep-shelf" environment which is separated from the deepest part of the basin by a transitional basin slope (Figure 2.1) (Lineback, 1980; Barrows and Cluff, 1984; Beier, 1988). In the deepest part of the Illinois basin, the New Albany is characterized by black shales, which are thought to result from the presence of anoxic bottom waters. Interbedded black and green shales, which characterize the deep shelf sediments, however, are attributed to vertical fluctuations in the position of the oxic/anoxic boundary about the water column/sediment interface (Beier, 1988).

Stratigraphy and lithology

Clegg Creek, Camp Run, Morgan Trail, Selmeir and Blocher Members comprise the Devonian-Mississippian New Albany Shale in southern Indiana. Morgan Trail, Camp Run and Clegg Creek Members are addressed in this study. These units are composed of a finely laminated brownish black shales containing phosphatic and carbonate nodules, above an inter-bedded brownish-black shale/green mudstone which is overlain by another finely laminated black/brown shale. The stratigraphy of the vertical section studied and sampling intervals are presented in Figure 2.2. A detailed mineralogic description of each sample is listed in Appendix B.

Clegg Greek, Camp Run and Morgan Trail Members are similar in their mineral relations, but differ in amounts and types of organic and sulfide materials they contain (Cluff, 1980). Lithologically, all are dominated by quartz silt and illite, and contain minor amounts of chlorite and mica (Schaffer and Chen, 1981; Beier, 1988). Total organic carbon (TOC) and sulfur content decreases with depth in the section. Total organic carbon by weight in the Morgan Trail and Clegg Creek Members averages 5.3 % and 12.9 % respectively. In the Camp Run Member, total organic carbon ranges from 1 % in the greenish-gray to more than 11% in the black laminae. Organic matter in all three members is composed of 90-95% amorphous forms, and consists primarily of kerogen (Hasenmueller and Leininger, 1987). 5.5 % total sulfur is present in the Clegg Creek, 2.8 % in the Camp Run and 2.4 % in the Morgan Trail Member (Hasenmeuller et al., 1987). Pyrite occurs both as nodules and disseminated crystals throughout the section, forms laminae in the black shale, and fills burrows in the green shale (Beier and Hayes, 1989).

Fossils of pelagic organisms such as conodonts, fish debris, Tasmanites, and Stylionina, are present in all three units. Benthic forms are rare, and when present, appear to have been transported from a more oxygenated environment (Beier, 1988). Shallow burrows in the green shale laminae commonly penetrate the underlying black shale in thinly bedded intervals (Jordan, 1985).

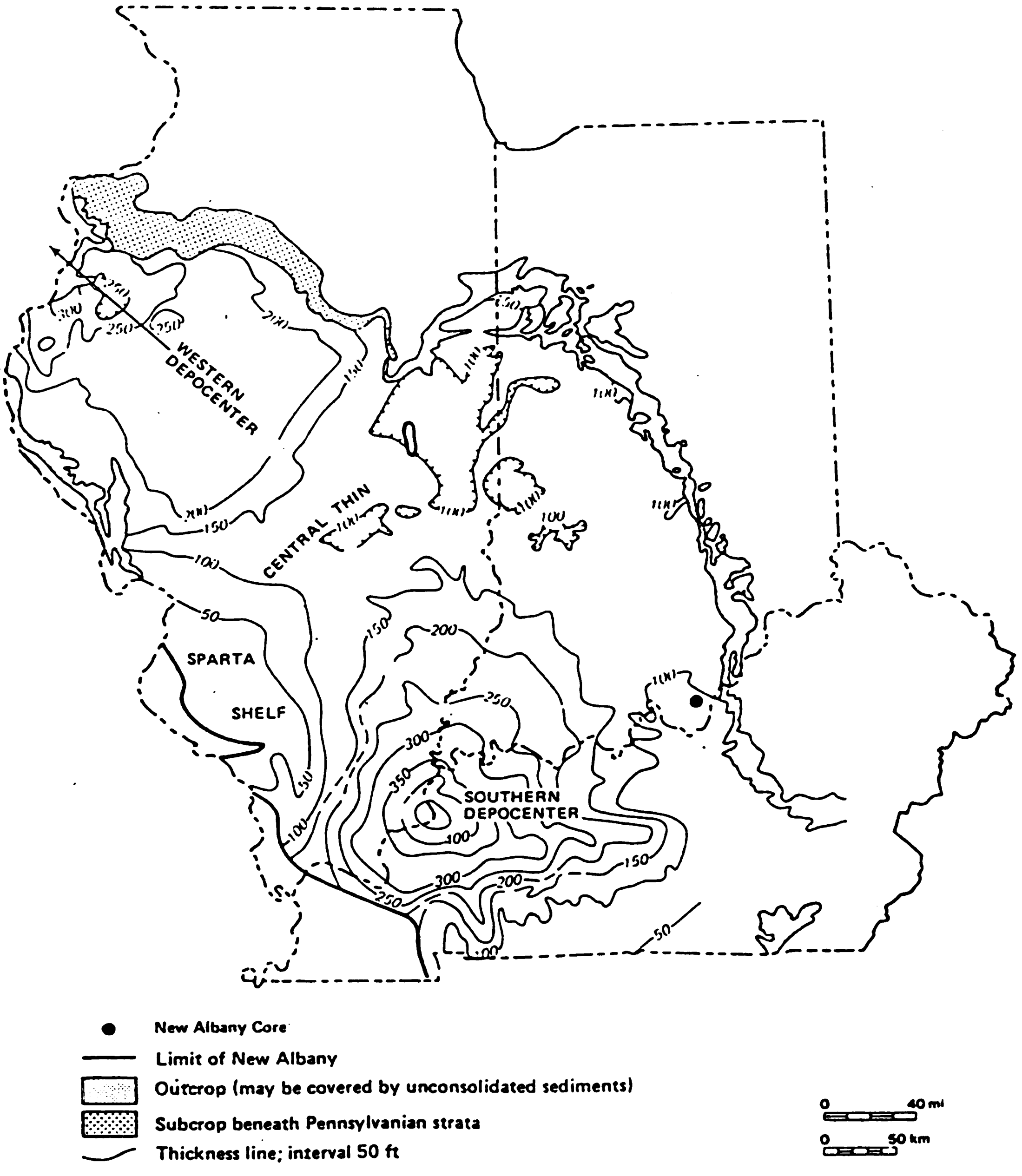


Figure 2.1 Geologic setting and location of core samples used in this study (modified from Cluff, 1980)

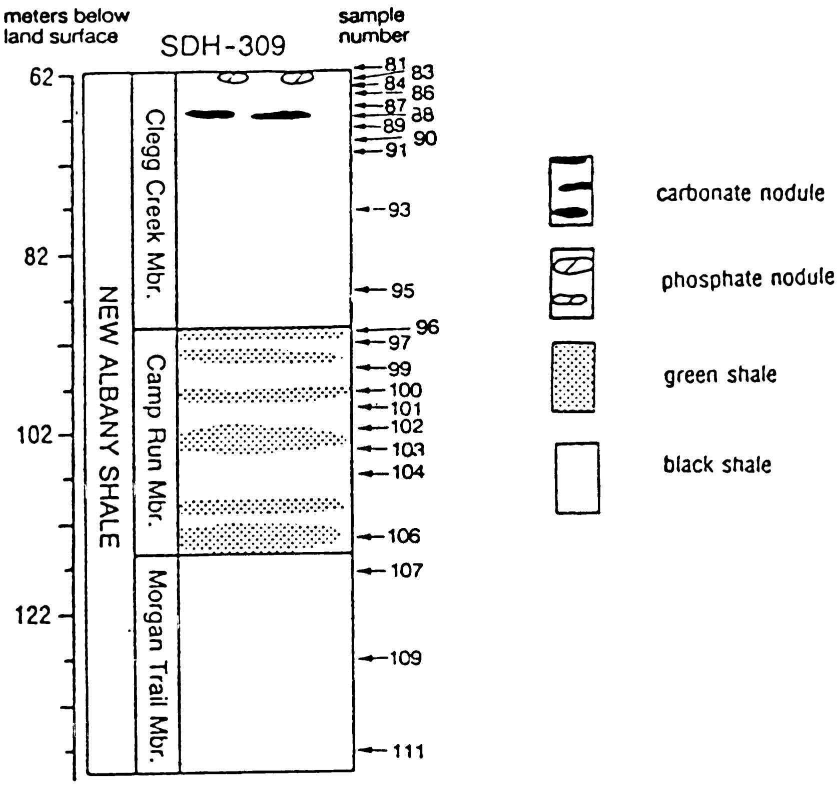


Figure 2.2 Stratigraphic section of the Clegg Creek, Camp Run and Morgan Trail Members of the New Albany Shale with positions of samples taken for this study (modified from Beier, 1988).

Paleoredox interpretations

Paleochemical conditions in sediments and bottom waters associated with the New Albany Shale have been interpreted based on lithologic, geochemical, and isotopic data, in addition to faunal assemblages. Organic-rich/phosphatic black shale, such as the Morgan Trail and Clegg Creek Members, is typical of sediments found in modern anaerobic environments where bottom waters contain less than 0.01 ml/l O_2 (Rhodes and Morse, 1972; Byers, 1977; Beier, 1988). Bioturbated green shale (e.g. Camp Run Member), is generally associated with dysaerobic conditions where 0.01 to 0.1 ml/l O_2 is present in the water column (Rhodes and Morse, 1972; Byers, 1977; Beier, 1988). Euxinic conditions during deposition in the Morgan Trail Member have been interpreted based on this information in addition to abundances of carbon and sulfur (Beier, 1988).

Formation of pyrite in 'normal marine' environments (where the redox boundary is at or below the sediment-water interface) takes place exclusively within the sediment and is limited by the amount of organic carbon available for sulfate reduction (Beier, 1988; Berner, 1980). A linear relationship between carbon and sulfur is representative of normal marine conditions, where the amount of sulfate reduced to sulfide is dependant on organic carbon in the sediment (Berner, 1984). Carbon versus sulfur plots for Morgan Trail and Camp Run samples show a linear correlation with a regression line intercept of zero. The linear trend implies non-euxinic conditions of deposition, and the zero intercept demonstrates that no sulfides formed in the water column due to an absence of organic carbon (Beier, 1988). Carbon versus sulfur plots for sediments associated with euxinic environments of deposition (where the redox boundary is in the water column) are characterized by a positive S-intercept, as the result of an addition to the sediments of sulfide formed in the water column. Sulfides formed in the water column are not coupled to the amount of organic carbon in euxinic environments in the sediment and therefore no direct relationship between C and S exists (Beier, 1988). Clegg Creek Member data demonstrated no correlation among carbon and sulfur abundances and are thought to be indicative of deposition in an euxinic environment.

Degree of pyritization (Raiswell and Berner, 1985) was also compared to total organic carbon (Beier, 1988) so as to discern samples in which pyrite formed exclusively in the water column from those in which pyrite formed in both the water column and in sediments (Beier, 1988). The degree of pyritization (DOP) is calculated using the equation:

$$DOP = Fe_{pyrite}/(Fe_{pyrite} + Fe_{reactive})$$

$Fe_{reactive}$ is Fe removed during reaction with HCl and Fe_{pyrite} is determined stoichiometrically from total sulfur measurements, based pyrite with a Fe:S ratio of 1:2 (Beier, 1988). Because the reduction of sulfate in sediments (i. e. the formation of diagenetic pyrite) is limited by the amount of organic carbon present, pyrite is positively correlated with organic carbon. High, uniform DOP values are characteristic of euxinic environments in which pyrite formation is thought to be limited by the amount of iron present in the water column (Raiswell and Berner, 1985). Positive correlation between DOP and organic carbon in Morgan Trail and Camp Run Members indicate carbon-limited pyrite and values for Clegg Creek suggest iron limited conditions throughout deposition.

Isotopic compositions of sulfur in the Camp Run and Morgan Trail Members range from del-^{34}S values of -5 to -20 o/oo· These values are characteristic of pyrite formed in a marine system in which the supply of sulfate was variable. del-^{34}S values for the Clegg Creek Members range from -5 to -40 o/oo, and are lightest at the top of the unit. Extreme depletion of del-^{34}S (values ranging from -25 to -40 °/oo) in sulfides from the uppermost Clegg Creek Member is thought to represent conditions in which "infinite" amounts of sulfate were available and sulfides formed in the water column. The overall shift up section from heavy to lighter values for del-^{34}S is interpreted as the result of bottom water conditions growing progressively more anoxic from Camp Run through Clegg Creek deposition. The negative del value occurs because bacterial fractionation is greater in more productive euxinic environments

The presence of phosphate nodules, in addition to a distinct zone of metal enrichment and an increase in total organic carbon at the top of the Clegg Creek Member, also suggests the existance of anoxic conditions during Clegg Creek deposition. Early diagenetic phosphate formation is commonly associated with high productivity in modern marine systems (Burnett, 1977). Phosphates in the Devonian sediments are thought to have precipitated in organic-rich/phosphatic mud, where high rates of decomposition of organic matter occurred via sulfate reduction and released abundant amounts of phosphate. Large trace metal accumulations in the upper Clegg Creek Member are associated with phosphates and adsorption onto large amounts of sedimentary organic matter.

In conclusion, Morgan Trail and Camp Run Member sediments are thought to have been deposited in normal marine (oxic) conditions and the Clegg Creek Member is believed to represent a shift to anoxic bottom water conditions and/or to indicate higher productivity (Beier and Hayes, 1989). Oxygen is thought to have been present during deposition of the Morgan Trail Member, based on C/S relationship, but because evidence of benthic organisms is not found in the Morgan Trail the redox boundary is thought to have been at or just above the sediment water interface during Morgan Trail deposition (Beier, 1988). Alternating beds of black and burrowed green shale in the Camp Run Member, in addition to C/S and TOC/DOP. relationships indicate dysaerobic conditions during Camp Run deposition where the redox boundary fluctuated about the sediment/water interface (Beier, 1988). Distinctly different C/S, and TOC/DOP relationships, and the lack of benthic fauna in the Clegg Creek Member, imply deposition under euxinic conditions. A negative excursion in del-^{34}S values, and the occurrence of phosphate and enriched trace metal concentrations in the upper part of the Clegg Creek Member indicate higher microbial productivity during Clegg Creek deposition and further indicates the presence of anoxic conditions.

METHODS

Sampling and sample pretreatment

Powdered well core samples were provided by the Indiana Geological Survey in Bloomington Indiana. Twenty four lithologically distinct samples were collected from a longitudinally sliced core. The samples represent segments of the core ranging from 3 centimeters to 3 meters in length, and comprise a 57.7 meter section of Indiana Survey drill core #SDH-309. Sample numbers and stratigraphy are described in Figure 2.2. SDH-309 is located in Township 3N, Range 6E, section 16 (NE SW) in Floyd County, Indiana (Figure 2.2).

Samples were crushed and powdered with a ceramic plate crusher and mortar and pestle, and sieved to pass the 250 mesh size. Resulting powders were stored in glass vials and dried at 25 degrees C prior to weighing.

Separation of chemically reactive fractions

A series of selective chemical extractions were applied to the shale as a means of isolating metals associated with the chemically reactive hydromorphic phases. The procedure assumes that individual hydromorphic phases are effectively removed from the shale during a progression of successively harsher chemical reactions. Although specific mineralogic phases, (such as Fe oxides, carbonates, etc.) are targeted in each reaction, the reagents used are not, 100 % efficient at isolating discrete hydromorphic phases (Rapin et al., 1986; Chao, 1984; Martin et al., 1987; Patterson et al., 1986) For this reason "operationally defined" phases, determined on the basis of their reactive properties (exchangeable, weakly acid soluble, easy and moderately reducible, and easily and moderately oxidizable), rather than mineralogic phases will be emphasized in conclusions made from this work.

The extraction procedure used in this study is a modified version of that described by Tessier et al. (1979) and Gephard (1982). The method was originally designed for normal marine sediments, however, and was not intended for use on lithified black shale, which accumulated under reducing conditions. Because black shales are often associated with organic or sulfide materials which form under reducing conditions (Volkov and Formina, 1972; Patterson, 1986; Pryor et al., 1980, Lewan and Maynard, 1982), the method of Tessier et al. (1979) and Gephard (1982) has been modified in this study. Tessier et al.'s (1979) oxidizable phase, which considers metals associated with both organic and sulfide fractions, has been adjusted so that metals associated with organic and sulfides phases may be treated separately. The "easily oxidizable" phase targeted in this study is thought to extract metals from organic materials (Bremmer and Lees, 1949) and the "moderately oxidizable" phases is believed to represent sulfide minerals (Chao and Stanzolone, 1977). The technique used be Piotrowski considered both oxidizable phases as one phase, in complience with the technique used by Tessier et al. (1979)

The following extraction procedure was used:

Exchangeable: 24 ml. of 1 M $MgCl_2$ was added to 3 gms. of dry sample. The reaction took place at room temperature for 1 hour with continuous agitation. (Gepart, 1982; Tessier, 1979)

Weakly Acid Soluble: 24 ml. of 1 M NaOAc was added to the remaining sediment at room temperature for 5 hours with continuous agitation. (Gephard, 1982; Tessier,1979)

Easily reducible: 75 ml. of 0.1M NH_2OH Hcl in 0.01M HNO_3 reacted with remaining sediment at room temperature for 30 minutes with continuous agitation. (Gephard, 1982; Tessier, 1979)

Moderately reducible: Remaining sediments were reacted with 60 ml. of 0.04M NH_2O HCl in 25% (v/v) HOAc at 96 degrees C with occasional agitation for 6 hours. (Gepart, 1982; Tessier, 1979)

Weakly Oxidizable: 60 ml. 0.1M NaP_5O_7 was added to remaining sediments and allowed to reacted for 1 hour at room temperature (Bremmer and Lees, 1949).

Moderately Oxidizable: 3 gm. of $KClO_4$ crystals were added to the remaining solid along with 60 ml. of Hcl at room temperature. After 30 minutes the reaction was quenched with the addition of 60 ml. of distilled/deionized water, and the solution was centrifuged (Chao and Stanzolone, 1979).

The reactions were conducted in 250 ml. Nalgene™ polyethylene bottles. All procedures, except for the oxidizable reaction, were carried out in a N_2 glove bag so as to maintain an oxygen free environment and prevent formation of secondary oxides. Upon completion of each reaction, solutions were centrifuged at 1500 rpm for 5 minutes, and supernatants were extracted. Samples which required centrifuge speeds higher than the equipment permitted and which remained turbid after 30 minutes of centrifugation, were filtered with acid-washed, 0.45 micrometer Millipore ™ filters. Sediments were rinsed after each extraction with 25 ml. of distilled/deionized water, centrifuged for 5 minutes, and rinse water was extracted and discarded. The leachates were stored in acid washed Nalgene ™ polyethylene bottles and acidified to a pH of 2. During each reaction, a bottle of unreacted reagent was acidified and stored under same conditions as the leachates, in order to serve as a reference blank. Sediments remaining upon completion of each reaction procedure were rinsed twice with distilled/deionized water and dried at 25 degrees C.

Analytical techniques

Leachate Analysis

Determination of FRTE abundances in extractants was conducted using a Perkin-Elmer 5100 atomic adsorption spectrophotometer. Flame atomization was used for samples containing high metal concentrations and a graphite furnace was used to measure metals in low concentrations. Due to the highly acidic nature of some of the leachates, corrosion resistant nebulizer parts were installed in the flame apparatus during analysis of moderately oxidizable extractants. Scandium was not determined in this study due to its extremely low concentrations in all samples. Analysis of metals associated with the exchangeable fraction was not possible due to the viscous nature of the leachate.

Whole shale and residual solids analysis

0.5 grams of each sample were used in this analysis. Metal concentrations were measured in untreated shale samples and the residual material using X-ray fluorescence spectrometry (Rigaku, S-MAX). Fe, Mn, and Ti were determined from fused glass discs and Criss matrix adsorption parameters were used to correct the major element analyses. V, Cr, Co, Ni, Cu and Zn were analyzed from pressed powder pellets, and were concentrations were determined using linear regression on U.S.G.S. standards (Wilband, 1975). Matrix adsorption effects were corrected sing the Compton peaks, as on internal standards. U.S.G.S. standards used and their elemental abundances are listed in Appendix II.

High concentrations of metal sulfides contained in New Albany samples posed problems during glass wafer preparation. In order to prevent the sulfides from reacting with platinum in the fluxing crucibles, 2 grams of NH_4NO_3 (a sulfide oxidizing agent) was reacted with the sulfide (Claisse, 1989). NH_4NO_3 was added to pre-dried samples during the preheating step designed to determine loss of elements on ignition. Loss on ignition was determined from samples which were weighed before and after heating to 1000 degrees C for 5 minutes.

First row transition element abundance plots

Data are presented graphically, following the approach of Piotrowski (1991). "Coryell" type graphs (Coryell et al., 1963) are used (Figures 4.1-4.9) in which normalized element abundances are plotted on the y-axis and FRTE are listed along the x-axis. Normalization is carried out by dividing each element's concentration by that of a standard. The method allows extreme variability in natural elemental abundances to be eliminated, and subtle differences in metal abundances to be made apparent. A logarithmic scale is used to accommodate elements whose abundances vary by several orders of magnitude. In order to best detect metal distributions that correlate with paleoredox conditions, a standard for normalization was chosen that represents normal marine conditions during New Albany deposition. The Morgan Trail Member is thought to represent oxic conditions and average values determined for each metal from the Morgan Trail Member samples were used for normalization (MTAS).

RESULTS AND DISCUSSION

Absolute abundances of FRTE determined for the untreated shale (bulk) and residual and hydromorphic fractions are listed in Appendix E. Values for FRTE concentrations in the untreated shale are similar to those of other authors (Vine and Tourtelot, 1970; Tourtelot, 1979; Piotrowski, 1991), and show enrichment with respect to normal marine shale in V, Cr, Co, Ni, Cu and Zn (Wedepohl, 1968; Taylor and McLennan, 1985).

FRTE concentrations in hydromorphic and residual fractions are similar to those of Piotrowski (1991), who used a selective chemical attack scheme nearly identical to that implemented by this study. Relative amounts of FRTE in residual and hydromorphic fractions of the shale for both studies are calculated using the equation:

$$\%\text{ metal in a fraction or phase} = \frac{\text{metal concentration in a fraction or phase}}{\begin{array}{l}\text{sum of metal concentrations in}\\ \text{hydromorphic phases}^{+}\text{ residual fraction}\end{array}}$$

Percentages of FRTE contained in the 5 hydromorphic phases and residual fraction are listed in Appendix D for all samples. An average value per element was determined for each phase from data in Appendix D, and is summarized in Table 4.1.

Table 4.1 Average distributions of FRTE elements among hydromorphic and residual phases of the upper New Albany Shale (n=24) as percentages

Element	hydromorphic or residual fraction					
	WAS (%)	ER (%)	MR (%)	EO (%)	MO (%)	RES(%)
Ti	0.00	0.02	0.01	0.12	0.53	99.30
V	0.03	0.06	0.31	0.03	0.26	99.50
Cr	0.27	0.02	24.30	0.37	22.96	49.39
Mn	12.00	11.20	46.59	2.41	1.05	16.47
Fe	0.81	0.97	13.35	0.53	27.23	57.09
Co	10.08	3.86	19.74	1.61	44.14	19.37
Ni	3.55	1.66	9.21	0.88	52.34	32.16
Cu	3.46	0.20	7.78	25.57	60.71	2.32
Zn	4.57	1.41	10.13	3.55	75.54	4.79

WAS=weakly acid soluble, ER=weakly reducible, MR=moderately reducible, EO=easily oxidizable, MO=moderately oxidizable, RES=residual phases

The residual fraction contains highest concentrations of most of the elements (2-99%), followed by moderately oxidizable (0-75%), moderately reducible (0-26%), easily oxidizable (0-26%), easily reducible (0-11%) and weakly acid soluble (01-10%) phases. This result agrees with the finding of Piotrowski (1991), who reported highest amount of metals in residual material, (30-100%) followed by oxidizable (10-60%), moderately reducible (5-20%), weakly reducible (0-10%), and weakly acid soluble (0-5%) phases. Because the moderately oxidizable fraction of Piotrowski (1991) is thought to represent the sulfide minerals, qualitative comparison of the two data sets suggests that metals in both Devonian shales are partitioned similarly.

An evaluation of selective chemical extraction methods

To determine the efficiency of the selective chemical attack scheme in isolating metals associated with the hydromorphic phases of the shale, each element's concentration in the bulk shale (Appendix D) is compared to the sum of it's concentrations in residual and sum of hydromorphic fractions. Theoretically, an element's concentration in the bulk shale sample should equal the sum of its abundance in the residual and hydromorphic fractions concentration. Therefore, the degree of analytical or laboratory error can be approximated through examination of the difference between bulk metal and residual + hydromorphic metal concentrations. Differences were determined for each metal from the values listed in Appendix D, and are summarized in Table 4.2. Values are expressed as the relative percent difference between bulk and all other phases, and are calculated as follows:

$$\text{relative difference (\%)} = \frac{\text{(metal abundance in 5 hydromorphic phases)} + \text{(residual fractions of sample)}}{\text{metal abundance in bulk sample}} * 100$$

Table 4.2 Difference between metal abundance in untreated samples and sum of metals associated with separable fractions (in %)

Sample number	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
81	2	2	40	6	3	29	20	40	18
83	12	1	67	38	5	9	4	46	7
84	8	15	16	4	8	17	5	49	7
86	15	12	47	3	7	20	7	37	331
87	15	29	345	3	6	35	16	38	562
88	10	14	42	22	8	61	16	41	571
89	18	13	39	3	10	21	15	5	22
90	7	22	41	13	11	26	72	32	507
91	12	3	74	17	6	6	28	48	256
93	8	10	153	37	6	51	15	7	202
95	3	2	86	8	3	10	11	40	40
96	1	3	77	3	3	30	18	27	12
97	7	10	51	4	3	44	13	49	28
98	5	16	84	6	3	34	18	34	45
99	3	7	47	20	1	34	18	34	79
100	1	10	60	11	1	68	13	25	245
101	4	8	62	8	8	16	24	35	218
102	3	11	90	5	3	14	89	39	119
103	2	3	66	6	2	21	39	56	64
104	5	14	123	10	1	32	40	32	289
106	12	16	48	5	4	22	7	47	113
107	9	14	79	4	4	25	12	54	325
109	2	7	109	91	1	20	42	58	71
111	19	15	51	6	5	5	46	27	63

Using a 20 % standard margin of error established by previous authors (Martin, et al.,1987; Tessier, 1979; Piotrowski, 1991), erroneous values are obtained for several metals in this study. Acceptable results are obtained for Ti, V, Mn and Fe, however differences in Cr, Co, Ni, Cu, and Zn exceed 20%. Several factors may explain the discrepancy in Cr, Co, Ni, Cu and Zn values. In an examination of Appendix E, it is noted that concentrations of Zn, Co and Ni in several samples are much higher in the moderately oxidizable phase than in the bulk fraction. Since the abundance of any metal in a hydromorphic or residual fraction should not exceed its concentration in the bulk shale, errors in either analysis of the moderately oxidizable phase or the bulk fraction are implied. Values for the bulk fraction were compared to an

Inductively coupled plasma (ICP) analysis of "splits" from the same samples (Beier, personal communication). The results obtained in this study are similar to those of the ICP analysis, indicating that the source of error may be related to the analysis of the moderately oxidizable phase.

A possible cause of the error in moderately oxidizable analysis may be contamination of the leachates. The strongly acidic $KClO_4$-HCl reagents used in this experiment are extremely corrosive, and thus their effects on the polyethylene storage bottles were evaluated prior to conducting the experiment. Blank solutions were analyzed 1 day after the experiments and were found to contain no metals. The same samples were analyzed at the time of leachate analysis, however, and contained significant amounts of Ni, Co and Cr, may have been extracted from container walls during storage. The moderately oxidizable samples used in this study were stored for several months prior to analysis, and may also have leached metals from the walls of the containers.

While discrepancies in Co, Ni, and Cr may be attributed to the aforementioned problems with the moderately oxidizable fraction, the error in values for Cu may be related to instrumentation. Persistent problems were encountered during atomic adsorption analysis of Cu, which may be attributed to a faulty Cu cathode tube. The anomalous values for Zn are unaccounted for.

The procedural errors in analysis of the moderately oxidizable phase illustrate that caution must be used in interpretation of the hydromorphic phases. Because FRTE in the bulk and residual fractions were determined using XRF analysis, contamination is less likely and sound interpretations may be made using data from the bulk, residual and total hydromorphic fractions (see below) of the shale. Information derived from the selective chemical extractions is evaluated with caution in this report, due to the above-mentioned problems in the data for the moderately oxidizable phase.

First Row Transition Element abundance patterns

In the following discussion, FRTE data in bulk, residual and hydromorphic phases are presented in sets of 6 graphs. Each plot represents a group of lithologically similar samples that was determined from examination of Appendix A. Samples from the Clegg Creek Member have been separated into 3 groups based on high organic carbon and phosphate contents (samples #81,#83,and #84), unique calcareous, brecciated appearance (samples #87 and #89), and general black shale lithology (#86, #88, #89, #90, #91, #93, #95). Camp Run samples are divided into two groups: those composed dominantly of black shale (#97, #99, #101, #104, #106) and those containing interbedded green/black shale (#96, #98, #102, #103). Morgan Trail samples are plotted as a single group because little internal variability occurs among samples.

Metal distribution:
XRF analysis

Bulk Shale

First row transition element abundances in bulk shale samples are presented in

Figure 4.1. The patterns for the 3 Clegg Creek Member groups (Figures 4.1a-4.1c) differ from each other, while Camp Run (Figures 4.1d,e) and Morgan Trail (Figures 4.1 f) patterns are similar in appearance. Samples in the organic-rich/phosphatic Clegg Creek group (Figure 4.1a) are enriched with respect to MTAS in V, Cr, Ni, Cu and Zn. Slight enrichment of Mn, Fe and Co is seen in sample #81, and concentrations of Ti in all organic-rich/phosphatic samples, and Mn, Fe, and Co in samples #83, and #84 approximate MTAS concentrations. Calcareous Clegg Creek samples (Figure 4.1b) are depleted with respect to MTAS in Ti, V, Cr, Cu and Zn, and enriched in Mn, Fe, and Co. Ni is enriched in #87 and depleted in #89. The black shale samples of the Clegg Creek Member (Figure 4.1c) contain Ti, V and Cr, concentrations which are similar to, or slightly depleted with respect to MTAS. Iron, Co, Ni, and Cu are enriched with respect to MTAS in this group and Mn, and Zn concentrations vary with respect to MTAS.

Plots for the interbedded green/black shale (Figure 4.2d), and the black shale (Figure 4.2e) Camp Run groups are relatively similar to each other. Concentrations of Ti, V, and Cr are nearly the same for the 3 groups, while Mn, Fe, Co, Ni, Cu and Zn abundances vary slightly among Camp Run samples. The Morgan Trail patterns (Figure 4.1f) plot as a straight line with a bulk shale/MTAS ratio of 1.

The difference in pattern shapes appears correlative with the shift in redox conditions assigned to the 6 sample sets. Patterns for Morgan Trail and Camp Run Members, which represent more oxic depositional conditions (Beier, 1988) (Figures 4.1a-4.1f) are similar to each other, and different from the Clegg Creek Member samples (Figure 4.1a-4.1c) which represent more anoxic conditions. This suggests

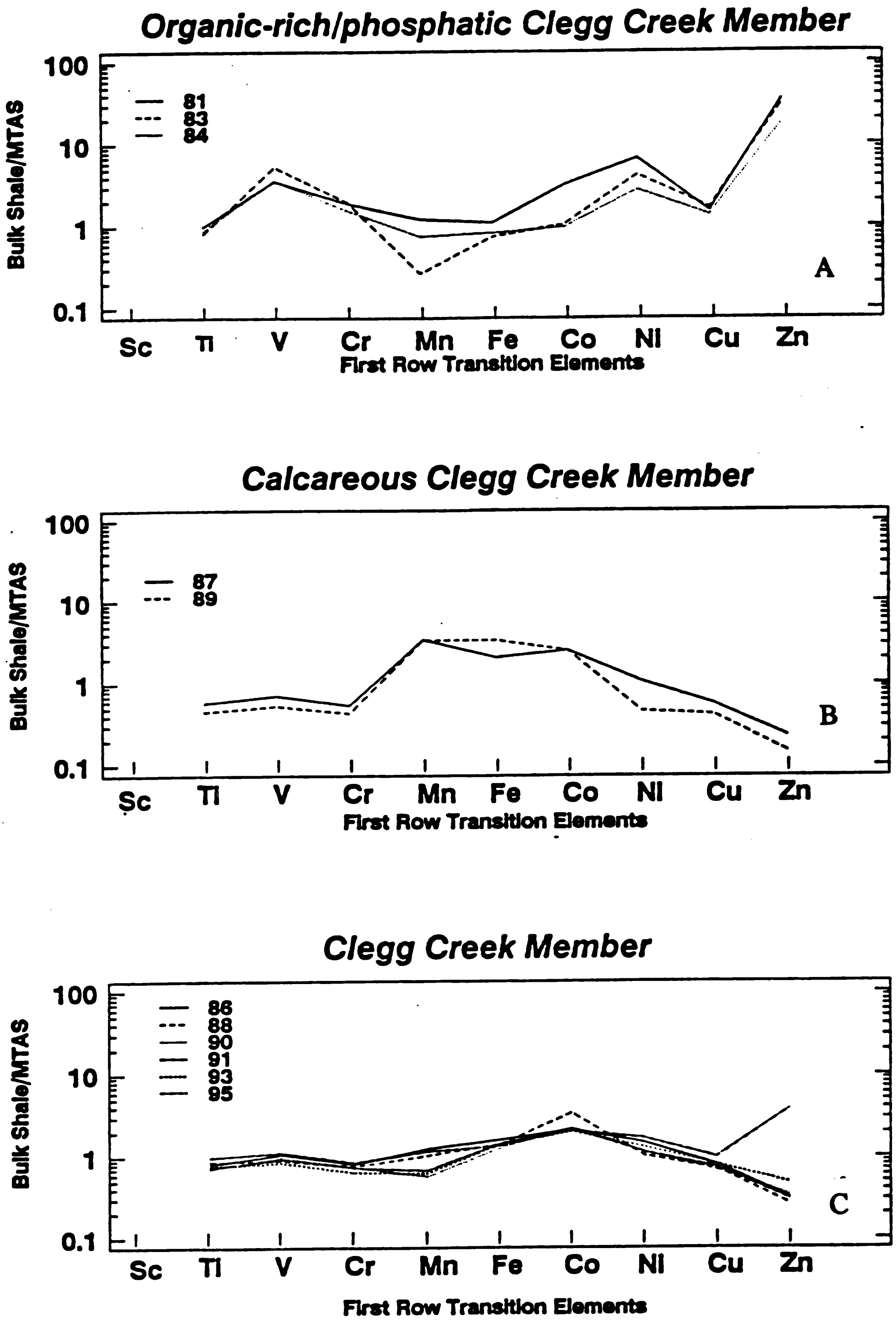
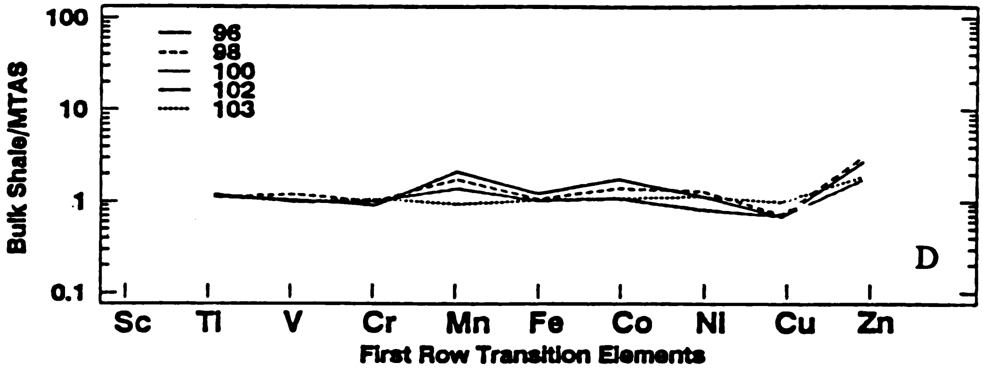
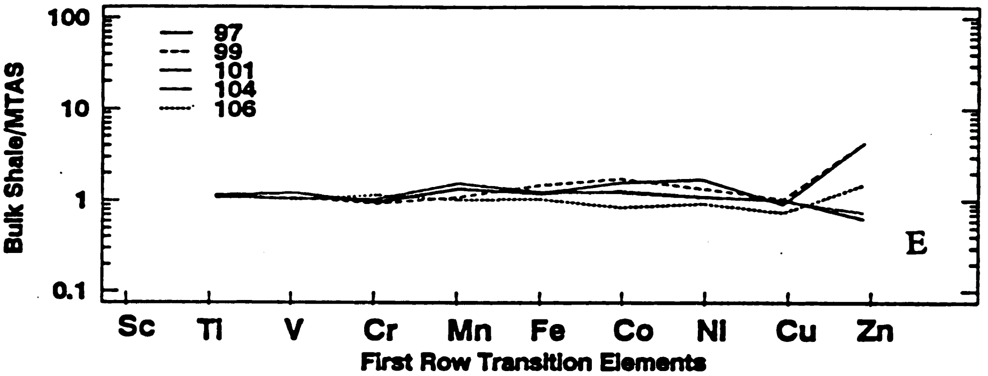


Figure 4.1 First row transition element abundances in bulk shale samples: a.) organic-rich/phosphatic, Clegg Creek Member samples; b.) calcareous, Clegg Creek Member samples; c.) black Clegg Creek samples d.) Interbedded green/black Camp Run Member samples e.) black Camp Run Member samples f.) Morgan Trail samples.

Interbedded green/black Camp Run Member



Camp Run Member



Morgan Trail Member

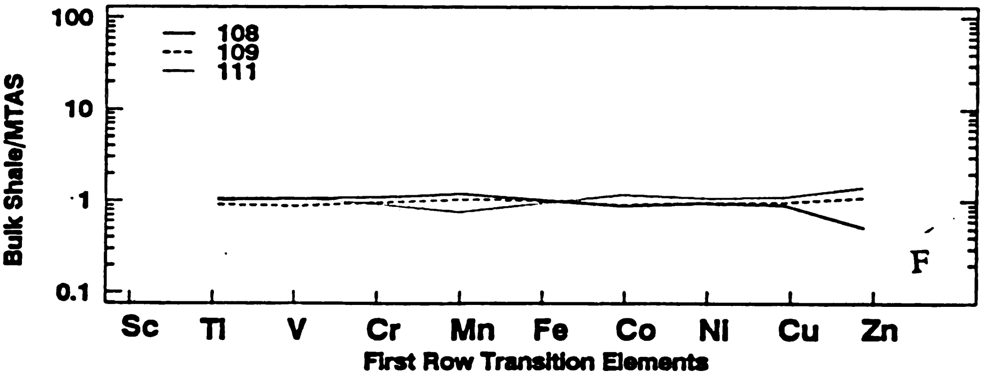


Figure 4.1 First row transition element abundances in bulk shale samples: a.) organic-rich/phosphatic, Clegg Creek Member samples; b.) calcareous, Clegg Creek Member samples; c.) black Clegg Creek samples d.) Interbedded green/black Camp Run Member samples e.) black Camp Run Member samples f.) Morgan Trail samples.

that different chemical controls on FTRE distribution exist in oxic than in anoxic environments. Although Camp Run (Figures 4.1d and 4.1e) and lower Clegg Creek shale samples (Figure 4.1c) have similar black shale lithologies, patterns for the two groups look different. The contrast implies that the pattern shapes may be controlled by redox conditions and not by lithology.

The Camp Run Member is thought to have been deposited during a time period in which the redox boundary fluctuated about the sediment water interface (Cluff, 1980). It has been proposed, as mentioned earlier, that such shifts may be reflected in alternating layers of green and black shale of the Camp Run Member (Beier, 1988). FRTE abundance plots in the bulk shale do not correlate with these predictions, in that patterns look the same for both green and black shales. This finding may indicate that: 1) fluctuations in the redox conditions were minor, and a general redox condition prevailed throughout Camp Run deposition, 2) samples were not carefully separated on the basis of color during sampling, or 3) subtle differences which occurred during sedimentation can not detected in an analysis of the untreated ("bulk") shale.

Differences in patterns displayed by the 3 Morgan Trail Group samples are consistent with the different lithologies in the group. Metal abundances in excess of those in MTAS are probably associated with high amounts of organic matter, which firmly hold their metals upon burial (Frost et al., 1985; Shaw et al., 1990). Insoluble sulfides, phosphates, or carbonates may also contribute to high concentrations of FRTE. This information suggests that pattern variations may be a function of lithology, and are independent of redox conditions.

The results confirm the assumption that information about original chemical environment of deposition can not be determined from analysis of the untreated (bulk) shale samples alone. In summary, both redox conditions and lithologies may influence trace metal distribution. Analysis of residual and hydromorphic phases is required in order to determine which of these factors controls FRTE distribution in black shales.

Residual fraction

Except for the organic-rich/phosphatic Morgan Trail samples, metal abundances and patterns for the 6 groups in the residual fraction are generally similar to each other. Abundances of Ti, V, Cr, and Ni in all residual plots are similar to those in the bulk samples, while concentrations of Mn, Fe, Co, Ni, and Cu are much lower in the residual fraction than in the bulk shale (Figure 4.1). The amount of each element in the residual fraction generally decreases with increase in atomic number for all plots in Figure 4.2, and reflects the decreasing lithophilic character of the elements across the group. The elements Mn-Zn are lower in concentration than Ti-Cr and vary slightly in their abundance. Due to their chalcophilic nature, these elements are more likely to be associated with the hydromorphic phase than the residual (Piotrowski, 1991). These results are similar to the findings of Piotrowski (1991).

Organic-rich/phosphatic samples (Figure 4.2a) contain Ti, V, Cr, Ni, Cu and Zn in higher concentrations than MTAS. Groups 4.2b-4.2f display Ti, V, and Cr concentrations which are approximately equal to those of MTAS. Manganese, Fe, Co, Ni, Cu and Zn are depleted in all samples with respect to MTAS, and vary

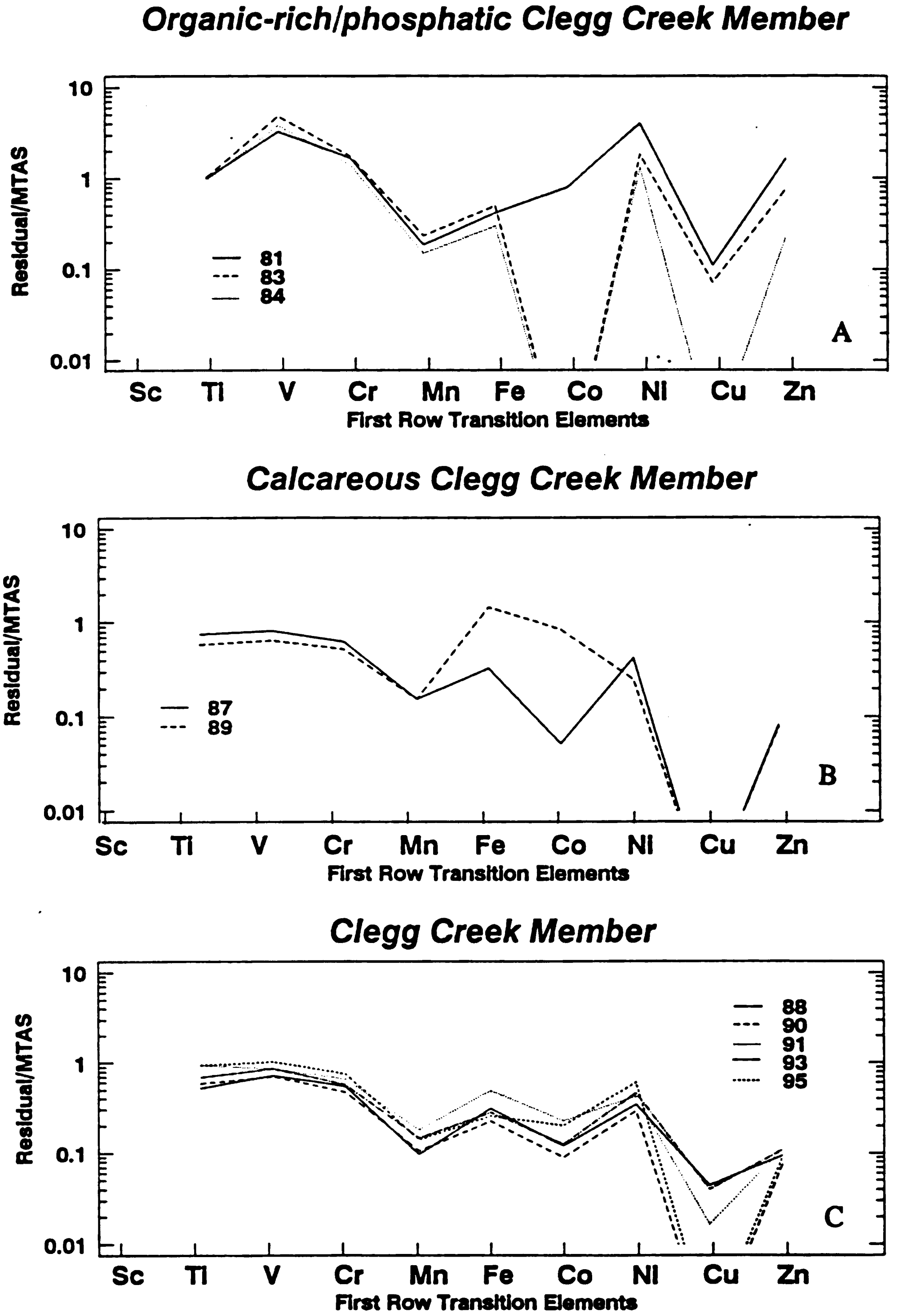
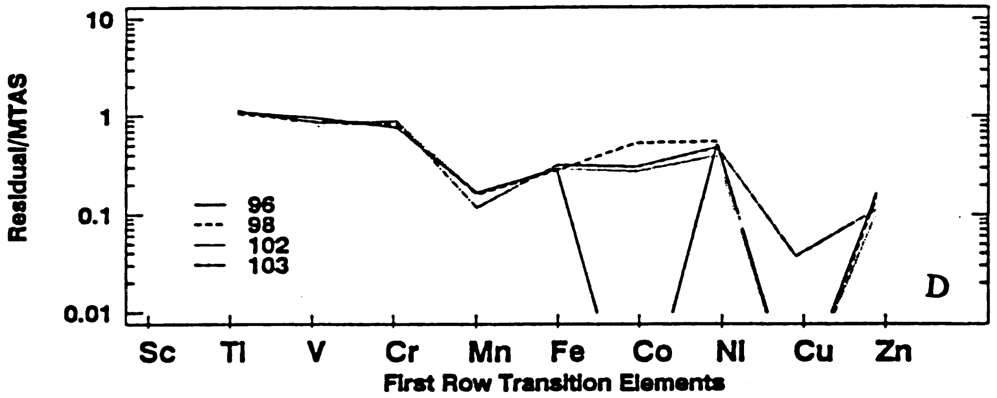
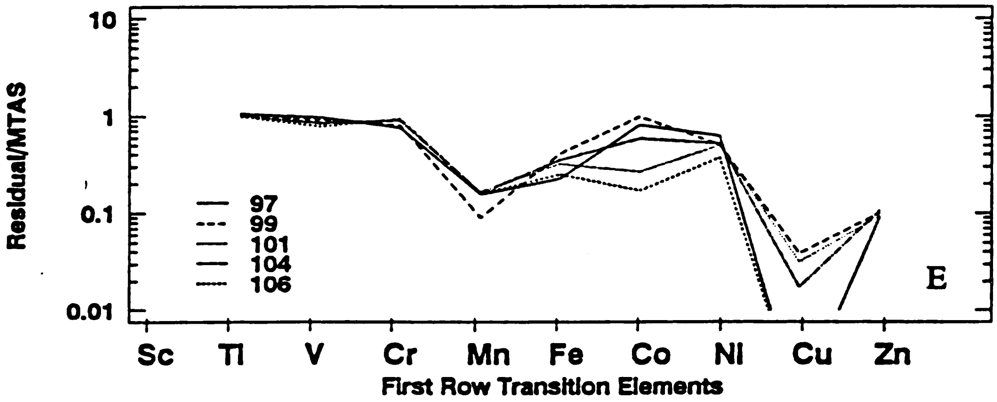


Figure 4.2 First row transition element abundances in the residual fraction: a.) organic-rich/phosphatic, Clegg Creek Member samples; b.) calcareous, Clegg Creek Member samples; c.) black shale Clegg Creek samples d.) Interbedded green/black Camp Run Member samples e.) black Camp Run Member samples f.) Morgan Trail samples.

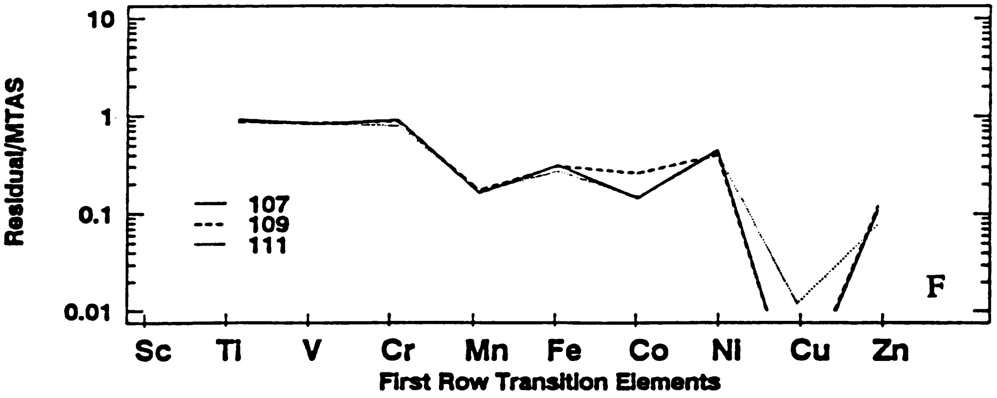
Interbedded green/black shale, Camp Run Member



Camp Run Member



Morgan Trail Member



slightly in their concentrations. The high concentration of metals in the organic-rich/phosphatic samples are likely to be associated with insoluble organic material (Frost and Chou, 1983) which was not removed during the extractions.

The similarity in the Ti-Cr part of the residual fraction patterns may be explained as a result of chemically consistent supply of detrital sediments during upper New Albany deposition. This hypothesis is supported by the observation that New Albany sediments are thought to have been continually supplied to the Illinois Basin by the Acadian highlands throughout late Devonian time (Frost et al., 1985).

The patterns do not appear to correlate with changes in redox conditions. Metal distributions in calcareous and black shale Clegg Creek samples, which are associated with anoxic conditions, are similar in appearance to those of the Camp Run and Morgan Trail Members, which represent oxic depositional conditions. Redox fluctuations proposed for Camp Run Member sediments are not indicated by the metal abundance patterns.

Total Hydromorphic Fraction

Trace metal concentrations in the total hydromorphic fraction are calculated as the difference between "bulk" metal concentrations and residual metal concentrations, because of the previosly discussed analytical errors in some of the individual hydromorphic phases. Values determined from this calculation are used in the following discussion, and are presented in Appendix D.

Figures 4.3a-4.3f demonstrate that the total hydromorphic fraction for all samples

(Figure 4.3) is highly depleted with respect to MTAS in Ti, V and Cr, and contains amounts of Mn, Fe, Co, Ni, Cu and Zn which are similar to MTAS. The six patterns for the hydromorphic fraction differ from those of bulk and residual fractions. Although abundances of Mn, Fe, Co, Ni, Cu and Zn in the total hydromorphic fraction are similar to those of the bulk shale, portions of the curve containing these elements do not exactly match those of the bulk fraction. Pattern shapes appear to be controlled by the lithologic character of the shales, as the organic-rich/phosphatic and carbonaceous Clegg Creek samples are distinctly different from other patterns.

Organic-rich/phosphatic Clegg Creek samples (Figure 4.3a) show an overall increase in metal abundances from left to right across the graph. The trend in organic-rich/phosphatic samples may be explained as a result of sequestering of the siderophile and chalcophile elements by phosphatic materials in the samples. Calcareous Clegg Creek patterns (Figure 4.3b) contain higher concentrations of Fe and Mn and are depleted in Ni and Cu with respect to other samples. The distribution of FRTE in the calcareous Clegg Creek patterns may indicate that higher concentrations of Fe and Mn-oxides exist the calcareous samples.

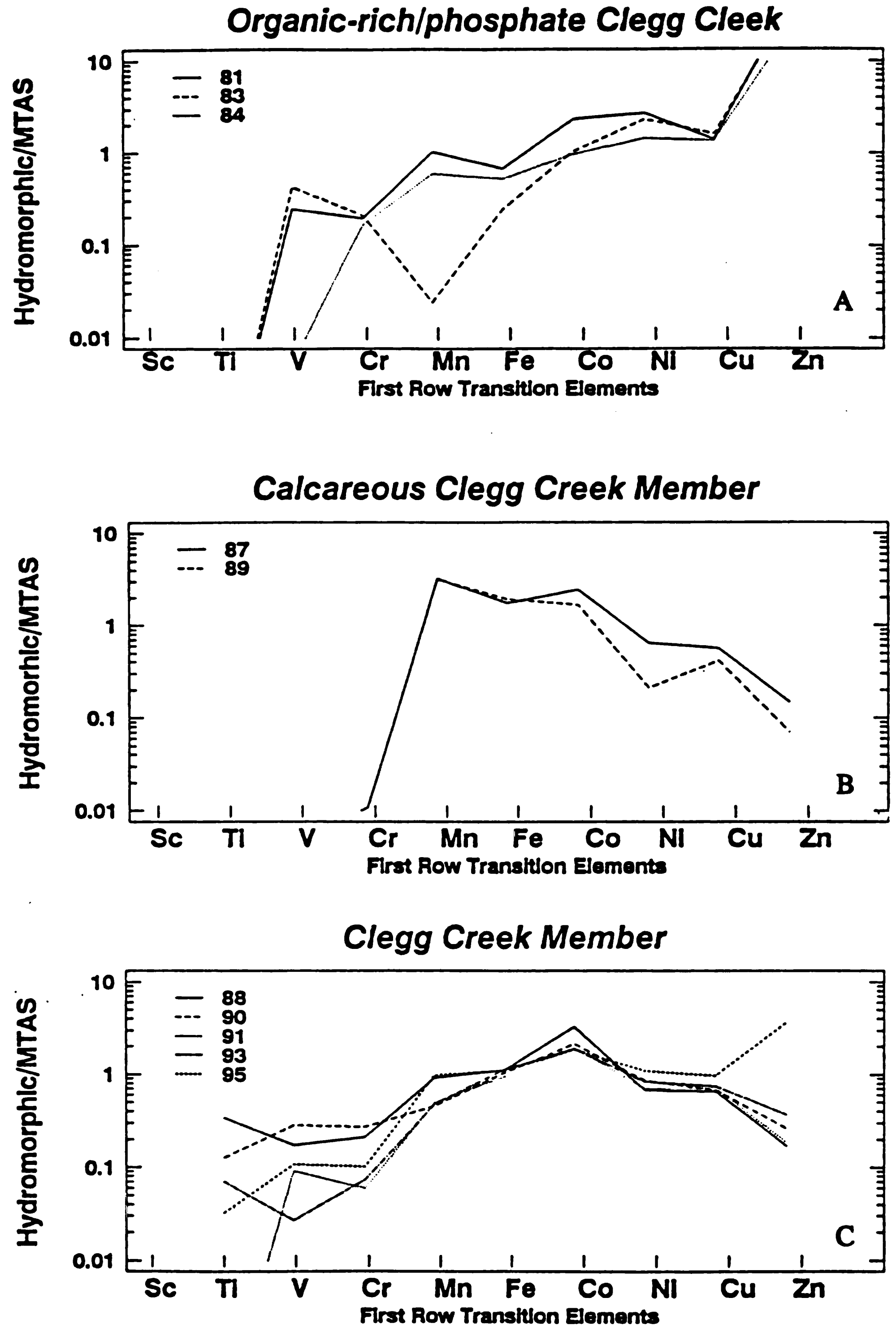
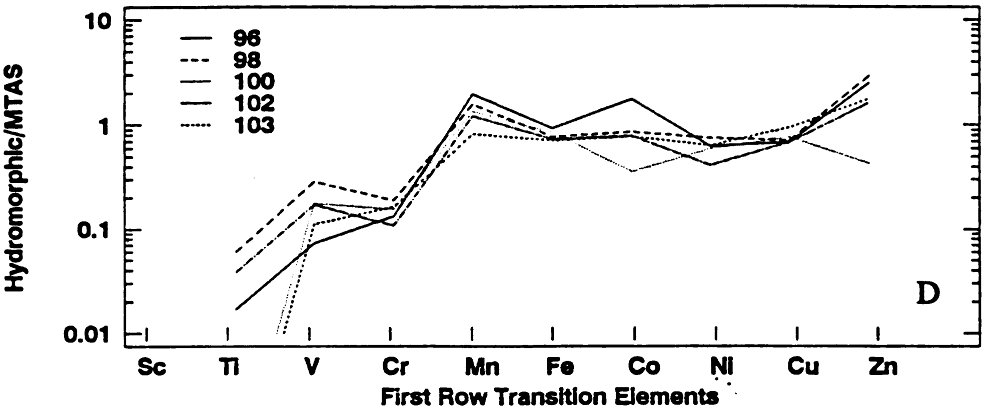
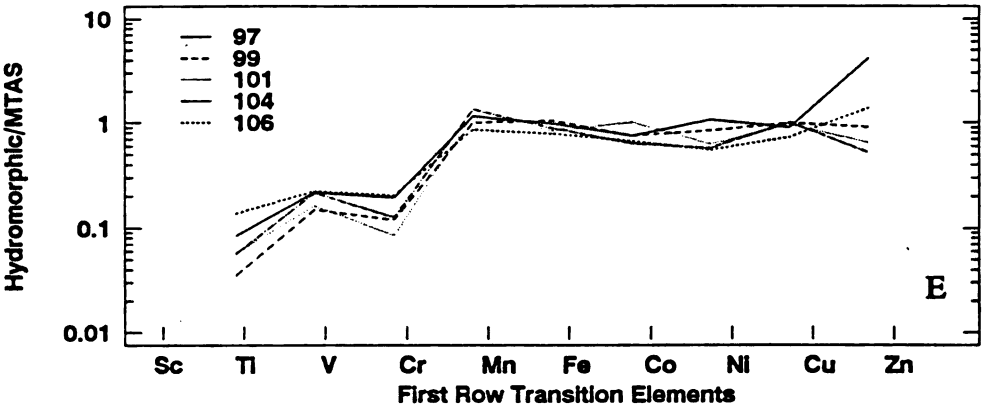


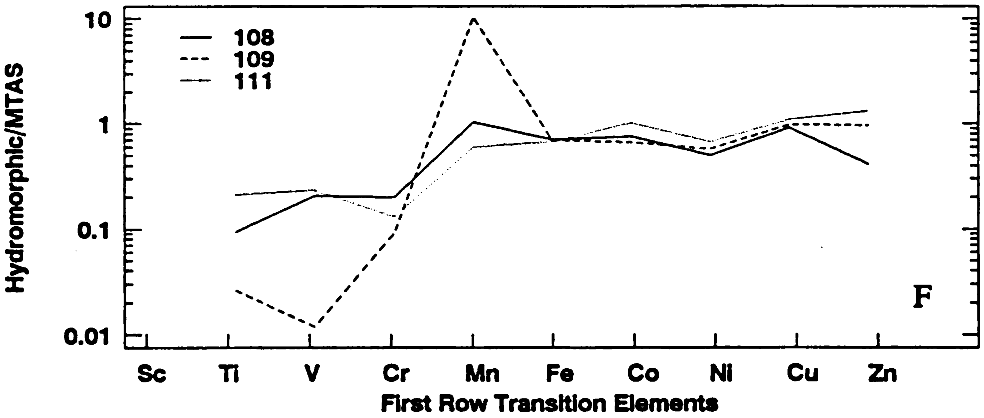
Figure 4.3 First row transition element abundances in total hydromorphic fraction: a.) organic-rich/phosphatic, Clegg Creek Member samples; b.) calcareous, Clegg Creek Member samples; c.) black shale Clegg Creek samples d.) Interbedded green/black Camp Run Member samples e.) black Camp Run Member samples f.) Morgan Trail samples.



Interbedded green/black Camp Run Member



Camp Run Member



Morgan Trail Member

Clegg Creek black shale samples are similar to those of Morgan Trail and Camp Run plots in Ti, V, Cr, Fe, Ni, Cu and Zn concentrations, but are enriched in Co and depleted with respect to Mn in the Clegg Creek samples. Because Co is a chalcophile element, it may indicate higher concentration organic material or sulfide in the Clegg Creek black shale.

Although no clear correlation between samples and redox regimes is apparent, correlation between patterns and redox conditions is implied by the similarity of Camp Run and Morgan patterns. Morgan Trail Members (Figures 4.3d-f) differ from those of Clegg Creek Member (Figures 4.3a-4.3c).

In summary, the shape of patterns in the bulk shale appears to be influenced by both hydromorphic and residual FRTE abundances for these metals. The bulk shale fraction appears to contain the most of the Ti, V, and Cr, while Mn, Fe, Cu, Co, Zn are predominantly found in the hydromorphic phase for all samples. The residual fraction appears to provide information regarding variations in the chemical nature of detrital sediments and insoluble organic materials. Scatter in FRTE abundances in some groups indicates that the amount of each metal sequestered by the hydromorphic phase may not have been consistent throughout deposition of the New Albany samples. The partitioning of FRTE among phases is discussed in the next section in an attempt to determine the relationship between FRTE and sedimentary redox conditions within individual hydromorphic phases.

Metal distribution in shale: partitioning analysis

In the following discussion, the hydromorphic phases are listed in order of their extraction during the selective chemical attacks.

Weakly Acid Soluble Phase

The weakly acid soluble extraction theoretically removes metals from the carbonate and phosphate minerals in the shale (Patterson, 1986), in addition to partially dissolving sphalerite (Patterson et al., 1986) and Mn oxides (Tessier, 1979). Similarities between pattern shapes for the organic-rich/phosphatic and calcareous groups in the weakly acid soluble and total hydromorphic plots (Figures 4.3a and 4.3b) implies that the weakly acid soluble phase exerts an important influence on the total hydromorphic pattern shapes for these groups. Although patterns for the lower Clegg Creek, Camp Run and Morgan Trail samples are not similar to those of the total hydromorphic phase, high concentrations of Mn, Co, and Ni found in the weakly acid soluble phase approximate those of the total hydromorphic fraction.

High phosphate and carbonate concentrations in the upper Clegg Creek Members (Figures 4.4a and 4.4b) appear to influence the metal abundance patterns. Plots of metal concentrations in organic-rich/phosphatic (Figure 4.4a) and calcareous Clegg Creek groups (Figure 4.4b) are distinctly different from those of the other 4 groups (Figures 4c-4g) and show relative enrichment of V, Mn, Co, Ni, Cu and Zn with respect to Ti, Cr, and Fe. Samples in groups 4.4c-f are similar in shape, and show enrichment of Mn, Co, Ni and Zn with respect to Ti, V, Fe, and Cu. Cu is highly

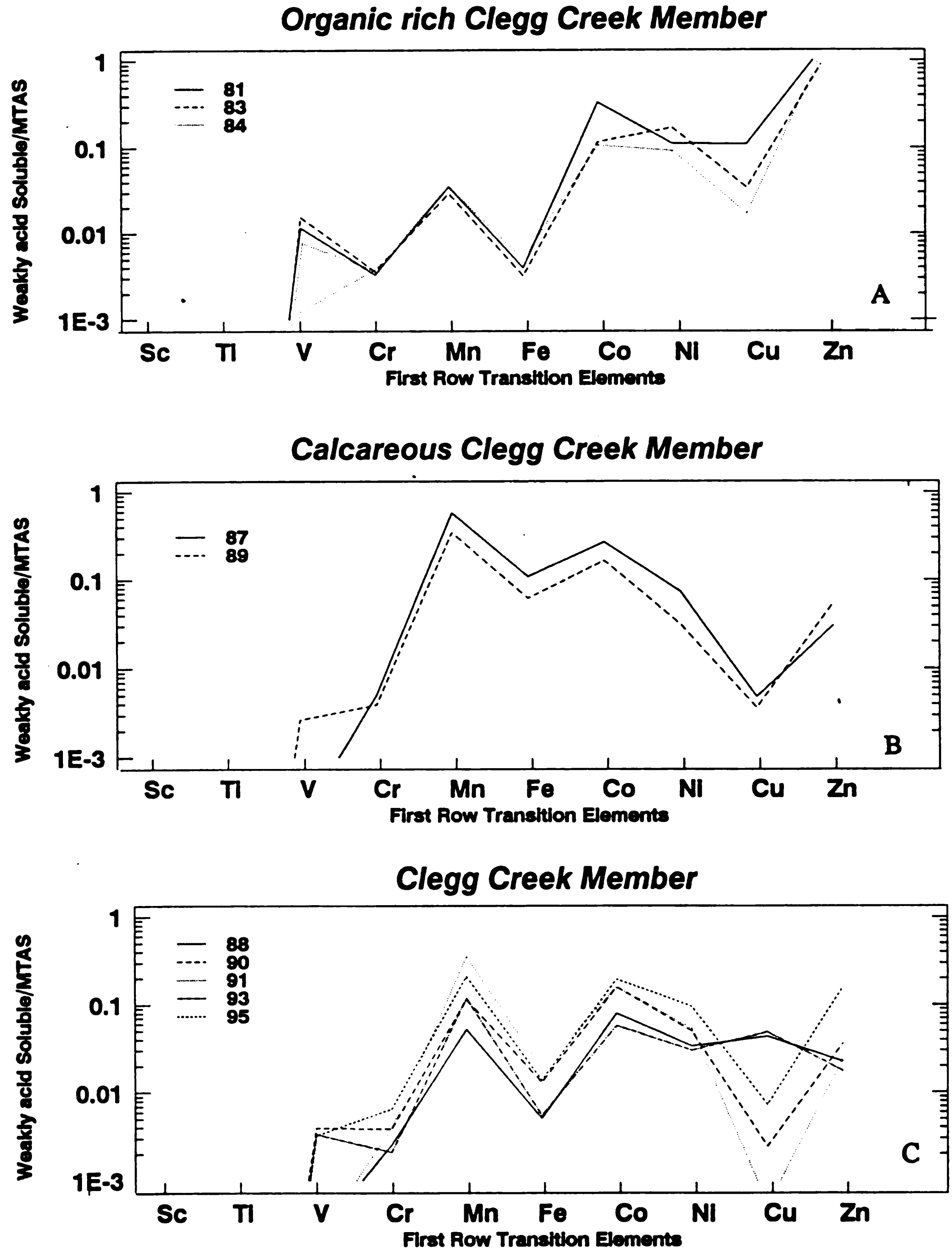
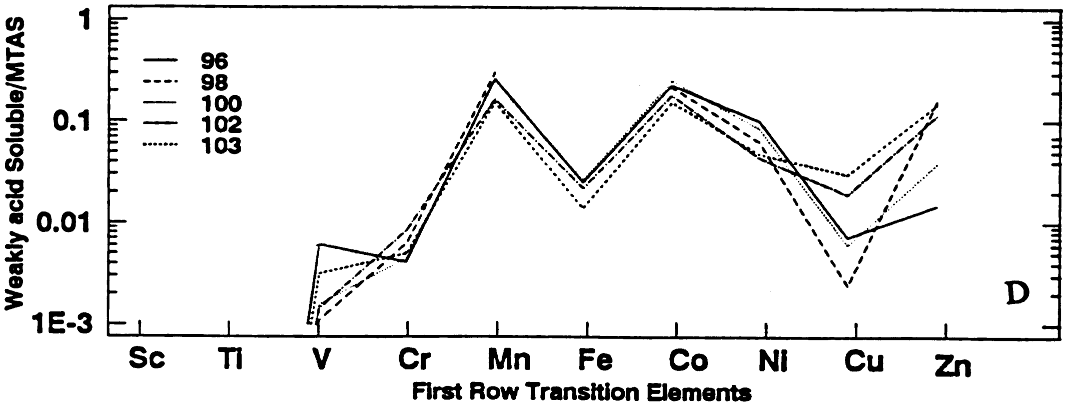
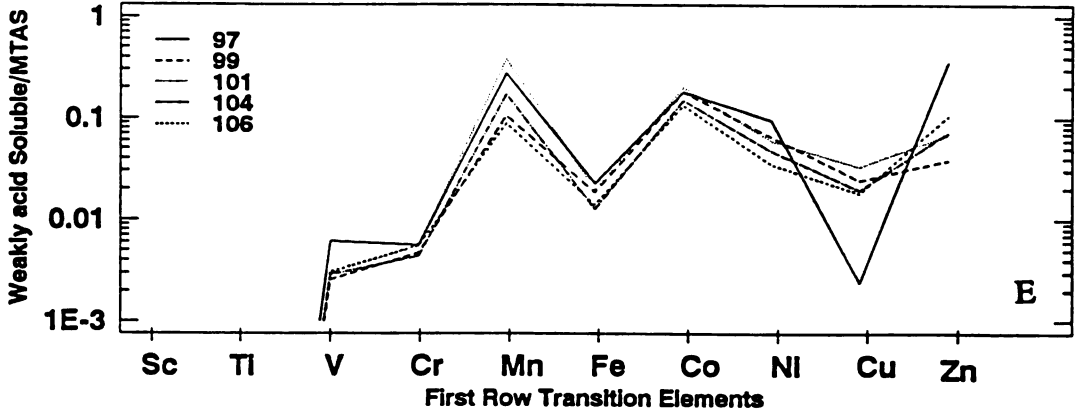
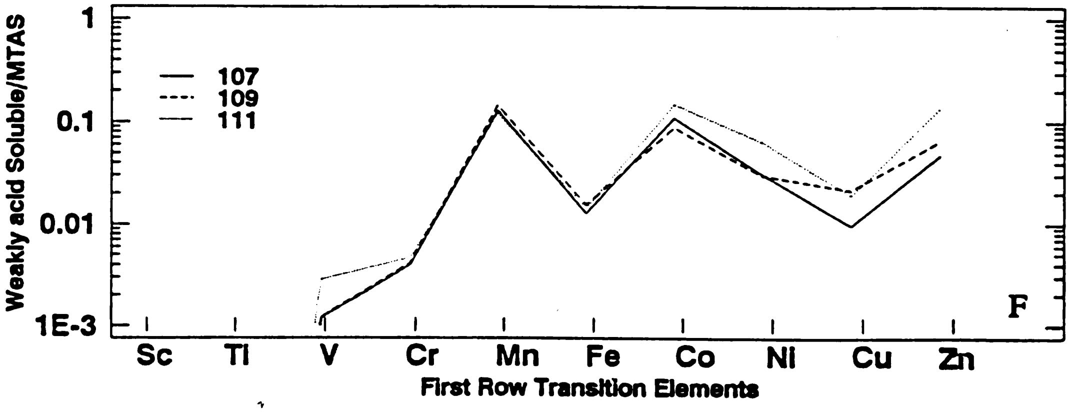


Figure 4.4 First row transition element abundances in weakly acid soluble phase: a.) organic-rich/phosphatic, Clegg Creek Member samples; b.) calcareous, Clegg Creek Member samples; c.) black Clegg Creek samples d.) Interbedded green/black Camp Run Member samples e.) black Camp Run Member samples f.) Morgan Trail variable in concentration among the samples.


Interbedded green/black shales, Camp Run Member


Camp Run Member


Morgan Trail Member

The high concentration of Mn in the calcareous samples may be the result of Mn substitution for Ca in carbonate, or due to partial dissolution of Mn oxide present in the sample (Piotrowski, 1991). High concentrations of Co are similar to those noted in the carbonate fraction of other studies (Kumar and Roonwal, 1987; Piotrowski, 1991); however Rapin and others (1987) suggest that Co and Zn in their black shale weakly acid soluble fraction may be the result of sphalerite dissolution. Although sphalerite is not described in the I.G.S. lithologic description of the section (Appendix A.), sphalerite-filled spores were discovered in some of the powdered samples upon and may explain the high concentration for Co in these analyses. The variability in amounts of Cu in the samples is difficult to explain based on the chemistry of Cu. Instrument problems associated with Cu, as described previously, are probably responsible for the discrepancy.

Because patterns for the black shale group of the Clegg Creek Member (Figure 4.4c) and the Camp Run and Morgan Trail samples are similar in appearance, the variations in patterns do not appear to correlate well with redox conditions. No variations in patterns are seen in the Camp Run samples to confirm fluctuation of the redox boundary during Camp Run deposition.

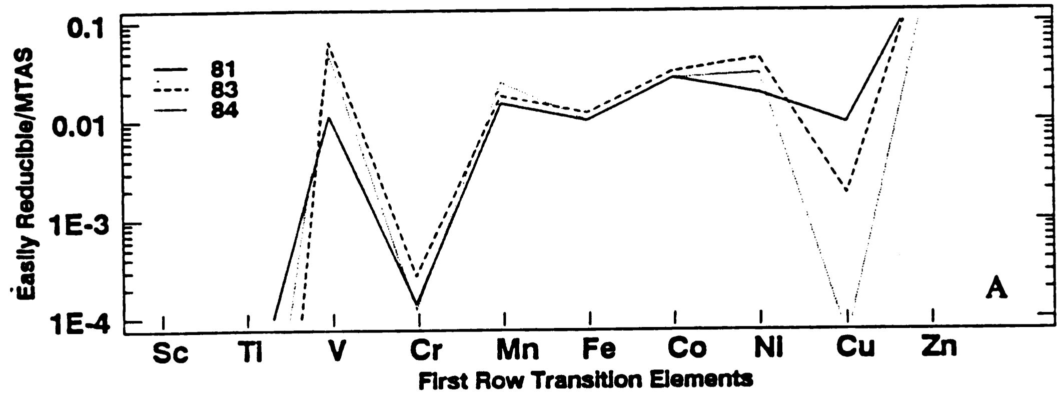
Easily Reducible Phase

Mn oxide is the targeted lithologic component in the easily reducible extraction. The metal abundance patterns representing the easily reducible phase (Figures 4.5a-4.5g) are quite different from the total hydromorphic patterns and do not appear to directly influence the shape of the total hydromorphic plots. The profiles also differ in appearance from those of the weakly acid soluble phase. Little variation in pattern shapes is seen among samples within each group.

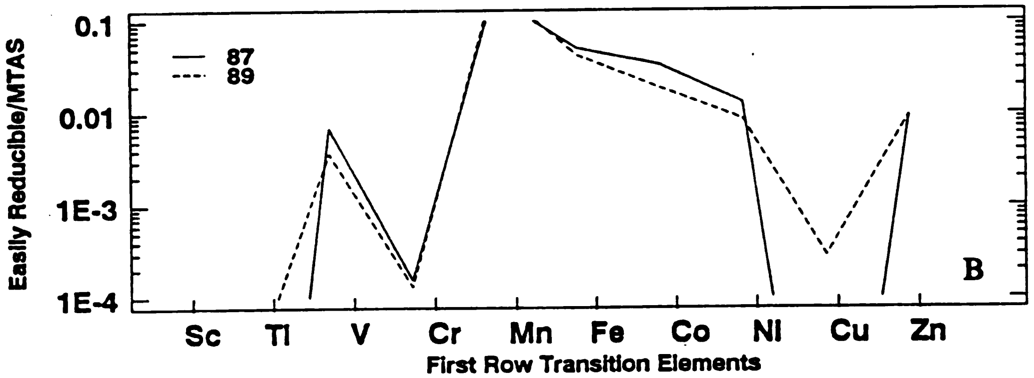
In general, patterns for the easily reducible phase among the 6 groups are relatively similar in appearance. Abundance patterns for Morgan Trail, Camp Run and #90, #91 and #95 in the Clegg Creek Members (Figures 4.5b,c,d,e) have similar shapes, while Clegg Creek samples show slightly varied forms. Morgan Trail, Camp Run and calcareous Clegg Creek samples are enriched in V, Mn, Fe, Co, Ni and Zn with respect to Cr and Cu, and calcareous Clegg Creek samples (Figure 4.5b) show slightly higher concentrations of Fe than is found in others groups. Ti is below detection limits for all samples. The abundance of all metals in black shale and organic-rich/phosphatic Clegg Creek groups is variable. The organic-rich/phosphatic samples contain higher amounts of V and Zn than do other samples.

Predictions made previously regarding the distribution of Co, Ni, Cu in the oxic sediments are not confirmed by these results. The hypothesis that Co, Ni, and Cu would only replace Mn in oxidizing conditions, and thus provide distinct differences in shapes of patterns for samples associated with oxic and anoxic conditions is not supported. Mn is found in higher concentrations in samples associated with the

Organic-rich/phosphatic Clegg Creek Member



Calcareous Clegg Creek Member



Clegg Creek Member

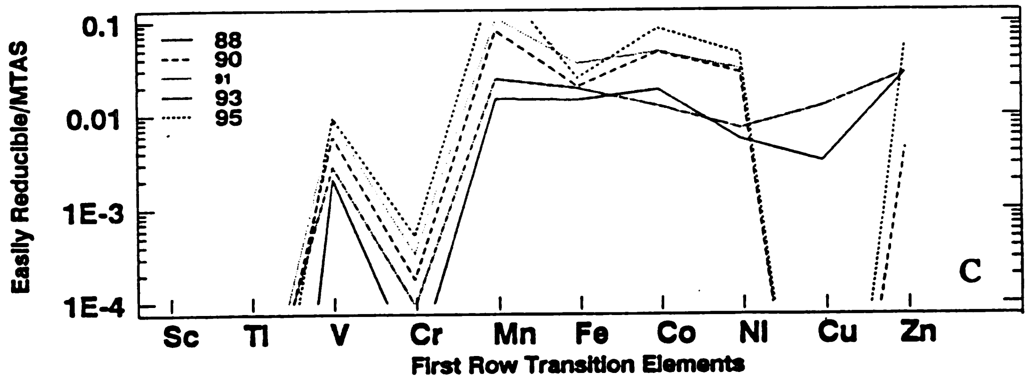
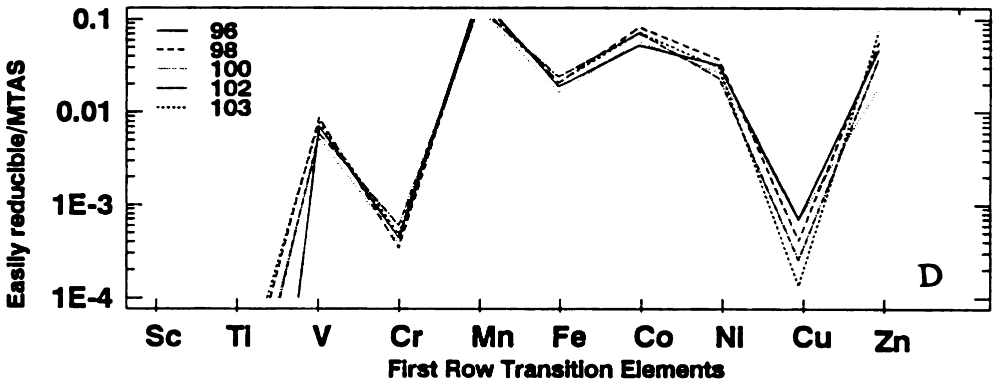
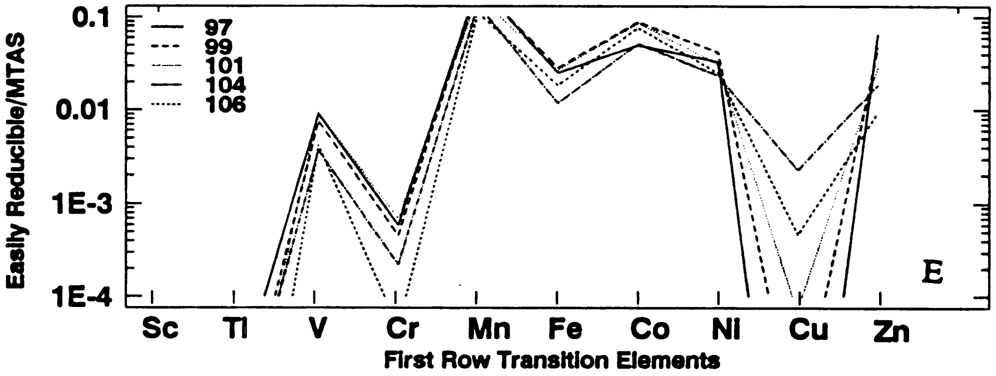
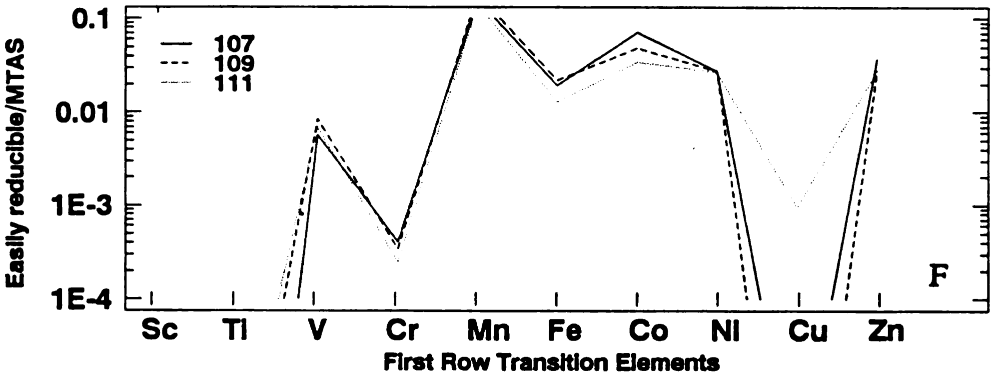


Figure 4.5 First row transition element abundances in easily reducible phase fraction: a.) organic-rich/phosphatic, Clegg Creek Member samples; b.) calcareous, Clegg Creek Member samples; c.) black Clegg Creek samples d.) Interbedded green/black Camp Run Member samples e.) black Camp Run Member samples f.) Morgan Trail samples.


Interbedded green/black Camp Run Member


Camp Run Member


Morgan Trail Formation

oxidizing sediments than it is in samples associated with reducing conditions, and the concentrations of Co, Ni, Cu are about the same in all samples.

Several explanations for the distribution of elements in the Mn-oxide fraction may be given. First, because they are not stable at low pH and pe conditions characteristic of anoxic environments, oxides may have never formed in the New Albany sediments. Also, any oxides which may have formed might also have dissolved as they were exposed to reducing conditions during burial (Shaw et al., 1990). If either case is true, FRTE signature associated with the anoxic sediment phase may in fact represent some hydromorphic phase other than the targeted Mn oxide, and additional materials may have been partially removed in the extraction.

A second possibility for the lack of correlation between redox conditions and metal distributions in the moderately reducible phase is that concentrations of Co, Ni, Cu may not have been present in the proper valance state to allow for substitution of Mn or Fe in the oxide phase. This may have occurred if the pH and pe conditions of the bottom waters were not high enough to allow the elements to exist in their higher valence states in the water column. The findings may indicate that anoxic bottom waters prevailed throughout New Albany deposition and that no shift in redox conditions took place.

An additional explanation for the FRTE distribution in the easily reducible phase lies in the diagenetic history of the samples. It is possible that the easily reducible phase has been overprinted by burial diagenesis and that some elements have been redistributed. In addition, the oxide phase analyzed in this study may have formed during late diagenesis as a near surface weathering product, and be unrelated to paleoredox conditions present during the Devonian (Piotrowski, 1991).

Moderately Reducible Phase

Iron oxides are targeted by the moderately reducible phase. The pattern shapes for the moderately reducible phase do not match the total hydromorphic fraction, however concentrations of Mn and Fe in calcareous Clegg Creek, Cr and Mn in other Clegg Creek samples, and Mn, Fe, Co, Ni are in the Morgan Trail and Camp Run samples approximate those of the total hydromorphic fraction. Although patterns associated with the moderately reducible phase and total hydromorphic fraction do not look alike, it appears that high FRTE concentration in the moderately reducible phases must contribute significantly total hydromorphic metal contents, based on metal abundances.

The moderately reducible patterns are similar to those of the easily reducible phase in that individual groups are consistent internally, however pattern shapes are not similar. The distribution of metals in the easily reducible phase differs from the other phases in overall pattern shapes and higher abundances of metals.

Camp Run and Clegg Creek groups are depleted in V, Mn and Cu with respect to Ti, Cr, Fe, Co, Ni and Zn. All metal abundances in Clegg Creek samples are variable. The organic-rich/phosphatic Clegg creek group contains higher concentrations of V and Ni than do the other Clegg Creek Member samples, and the calcareous samples are enriched in Cr and Mn with respect to the other samples.

The high concentrations of V and Ni in the organic-rich Clegg Creek samples

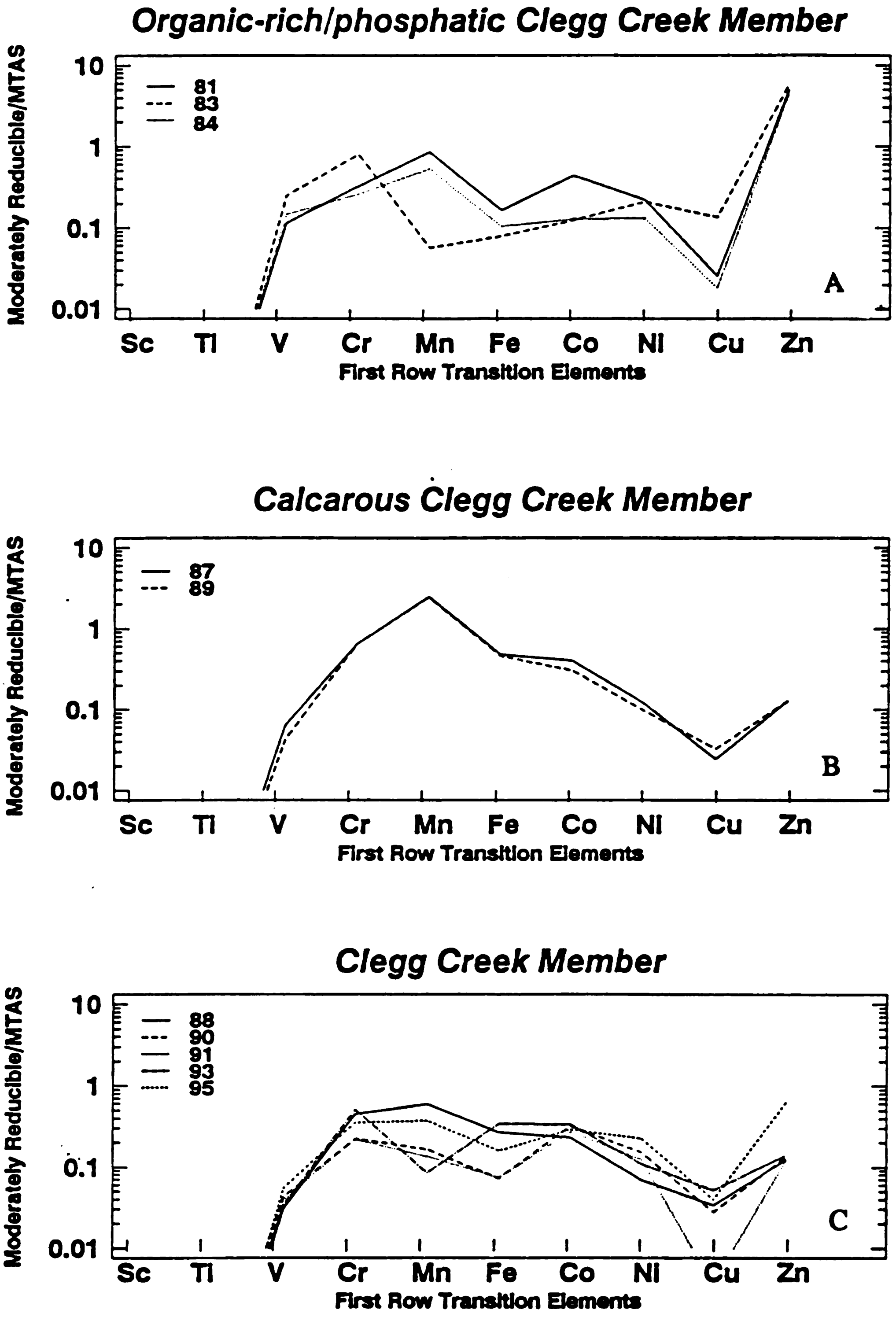
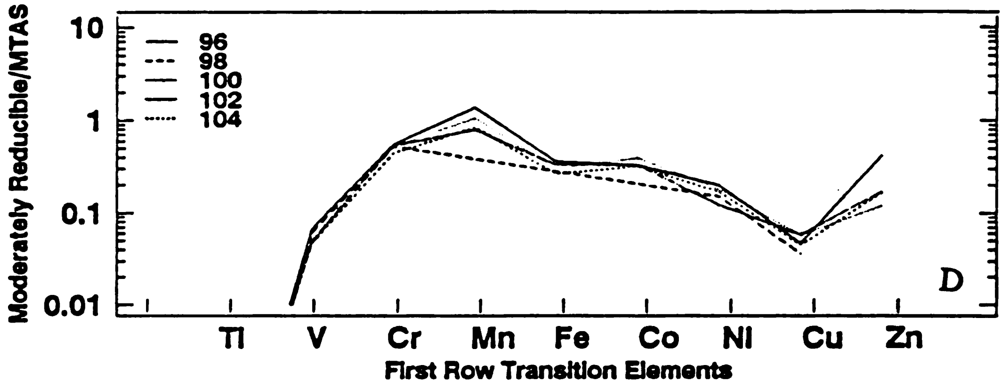
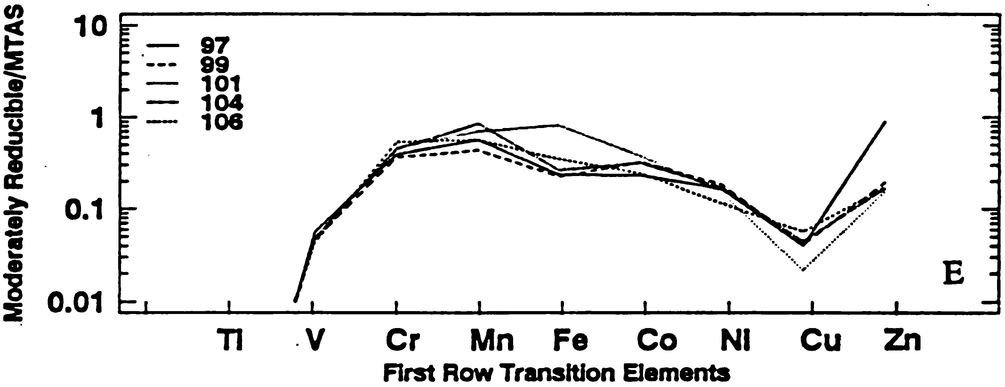


Figure 4.6. First row transition element abundances in the moderately reducible phase: a.) organic-rich/phosphatic, Clegg Creek Member samples; b.) calcareous, Clegg Creek Member samples; c.) black shale Clegg Creek samples d.) Interbedded green/black Camp Run Member samples e.) black Camp Run Member samples f.) Morgan Trail samples.

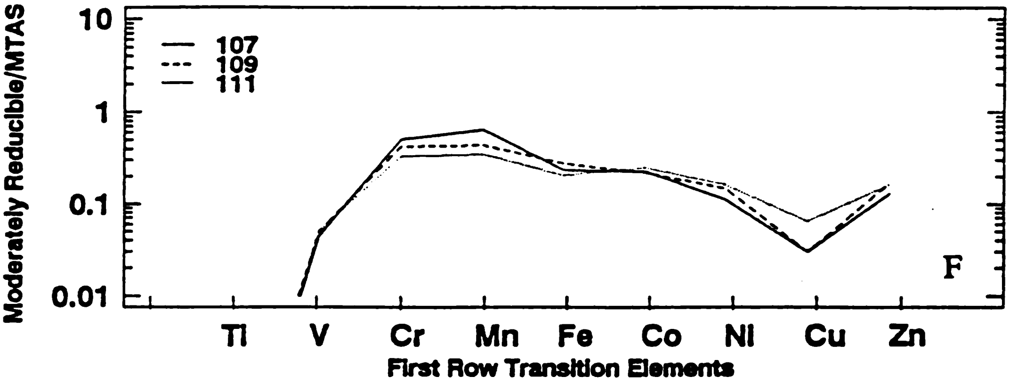
Interbedded black/green shale, Camp Run Member



Camp Run Member



Morgan Trail Member



may be the result of partial dissolution of organic materials. These elements are enriched only in the organic-rich/phosphatic samples, and no preference for V and Ni in Fe-oxides is indicated by CFT. High concentrations of Cr and Mn may be explained as associated with carbonate material which was not completely removed during the weakly acid soluble extraction.

The predictions regarding Co, Ni and Cu are not supported by the FRTE distribution in the moderately reducible phase. As in the Mn-oxides, Mn is enriched in the moderately reducible phase, and Co, Ni and Cu are not found in higher concentrations in oxic sediments than in anoxic sediments as expected. As discussed above, several explanations may be given for the outcome of these results. Because fractionation of Co, Ni, Cu in oxides was not detected, Co, Ni, Cu, concentrations are not expected correlated with redox conditions in any of the remaining hydromorphic phases to be discussed.

Redox conditions are not directly correlative with metal abundance patterns in the moderately reducible phase, however internally consistent patterns appear in groups representing oxic conditions (Camp Run, Morgan Trail and calcareous Clegg Creek) while pattern variability appears in samples related to anoxic conditions. No differences in pattern shapes is apparent in the black and interbedded green/black Camp Run groups.

Easily Oxidizable Phase

The easily oxidizable phase is thought to represent metals which are chelated or complexed by organic material. Although this extraction was designed for use in

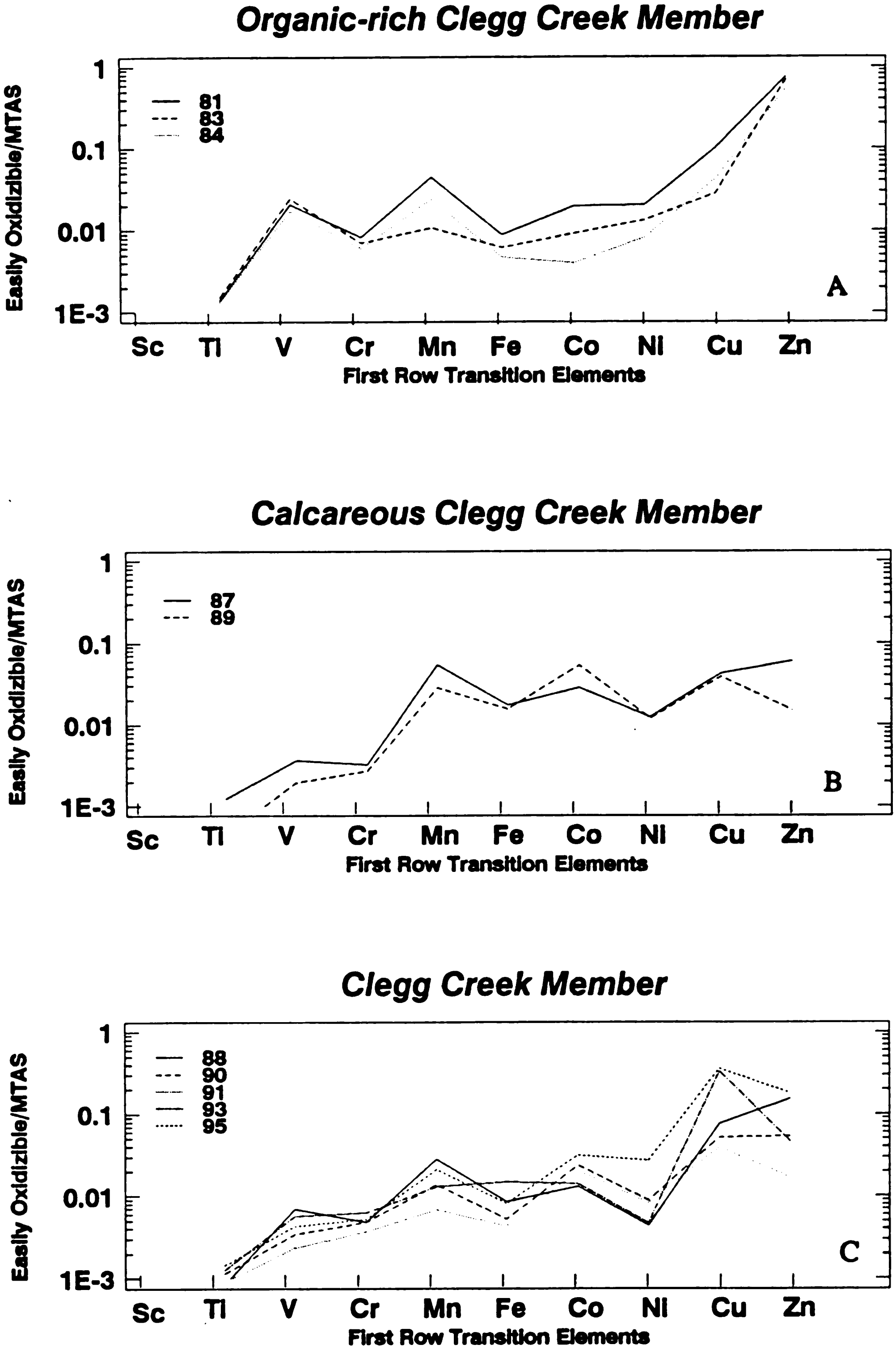
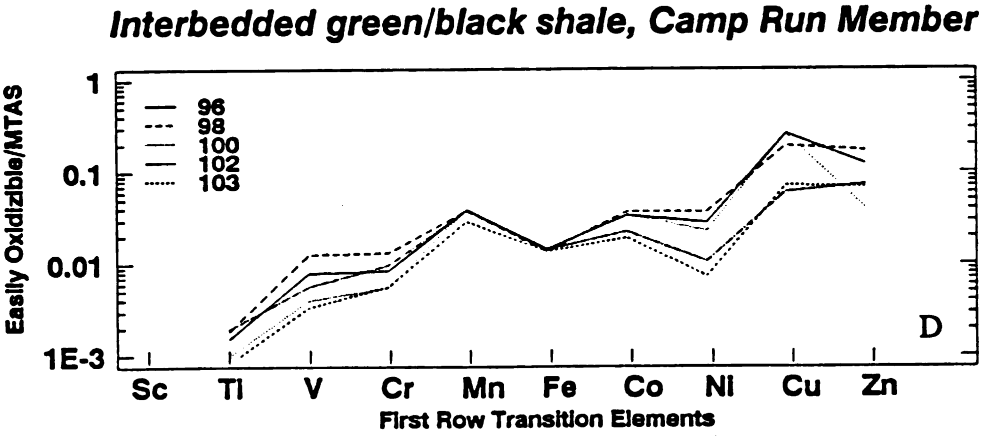
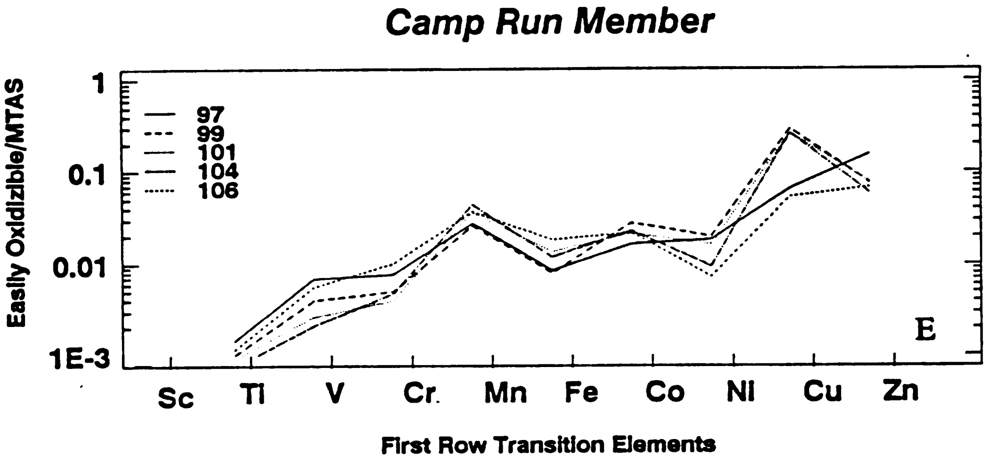


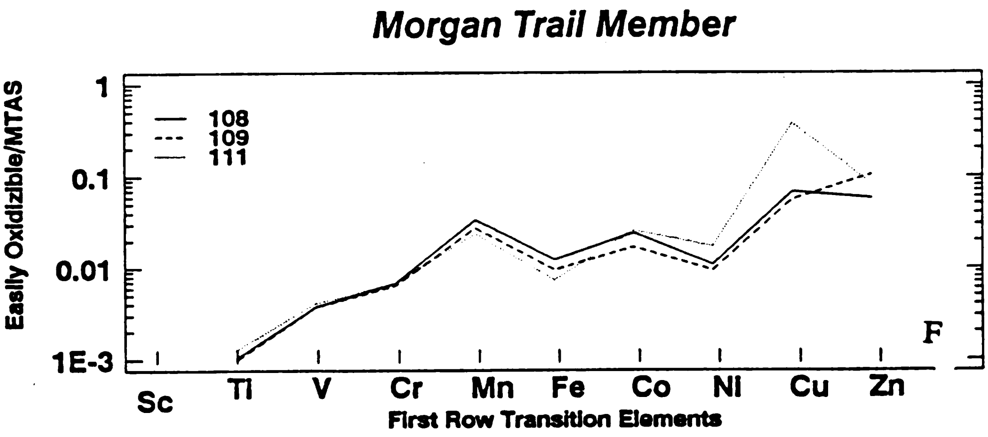
Figure 4.8. First row transition element abundances in the easily oxidizable phase: a.) organic-rich/phosphatic, Clegg Creek Member samples; b.) calcareous, Clegg Creek Member samples; c.) black shale Clegg Creek samples d.) Interbedded green/black Camp Run Member samples e.) black Camp Run Member samples f.) Morgan Trail samples.



Interbedded green/black shale, Camp Run Member



Camp Run Member



Morgan Trail Member

soils and unconsolidated sediments, it is believed to isolate a relatively labile component of organic matter in shales (T. Chao, personal communication). While most of the organic matter in the New Albany samples has been converted to kerogen (Hasenmeuller et al., 1987), it is thought that some metals remain in a relatively labile organic fraction (T. T. Chao, personal communication). This extraction theoretically removes any metals associated with such organic materials, although the exact nature of the organic forms is unknown.

Pattern shapes in this fraction (Figure 4.6) are distinctly different from those of the total hydromorphic fraction, and appear to contribute little to the shape of the total hydromorphic fraction patterns. They are also unique with respect to the other phases.

Metal abundance patterns for samples within the 6 groups (Figures 4.7a-4.7e) are relatively similar in appearance and show a progressive increase in FRTE concentration with increase in atomic number. Ti, Cr, Fe, and Ni are generally in lower abundance than V, Mn, Co, and Cu in most samples. Organic-rich/phosphatic Clegg Creek samples differ slightly from the other groups in that they contain higher concentrations of V and Cr than do other groups. Calcareous Clegg Creek samples contain less Cr than do other groups.

As predicted, concentrations of metals increase across group as a function of chalcophilic nature of the elements across the group. Slight variations in metal abundances occur in all groups and may be related to variations in types of organic matter or rates of productivity in the water column.

There is no correlation in the easily oxidizable fraction between samples and redox conditions, in that all patterns look similar. No difference in the patterns of the Camp Run Member is noted.

Moderately Oxidizable Phase

The moderately oxidizable reaction is believed to remove metals associated exclusively with sulfide minerals (Chao, 1977). The patterns are different in shape than those in the total hydromorphic plots. However, because anomolously large values have been detected for Cr, Co, Ni and Zn, a comparison with the total hydromorphic fraction may be meaningless for this fraction. The pattern shapes are unique with respect to other hydromorphic phases.

Metal distribution in all 6 plots, show relative depletion on Ti, V, and Mn with respect to the remaining elements. Minor differences are noted in the organic-rich/phosphatic Clegg Creek group. Concentrations of Zn and V in the organic-rich/phosphatic Clegg Creek are higher than in other samples.

Chalcophile and siderophile elements are enriched in the moderately oxidizable phase, as predicted. High concentrations of V and Zn in the organic-rich/phosphatic group may be attributed incorporation of the metals in the sulfide phase, or the result of partial dissolution the 'insoluble organic material'

Patterns do not appear to correlate with redox conditions, because with the exception of the organic-rich/phosphatic samples, all plots look alike. Variations in fluctuating redox boundary of the Camp Run member are not indicated by differing patterns.

Because the patterns for this phase are different in appearance than those associated with the easily oxidizable phase, it appears that the separation of the two phases was successful. Despite problems encountered during laboratory analysis of the moderately oxidizable metals, relatively consistent patterns are derived for the phase.

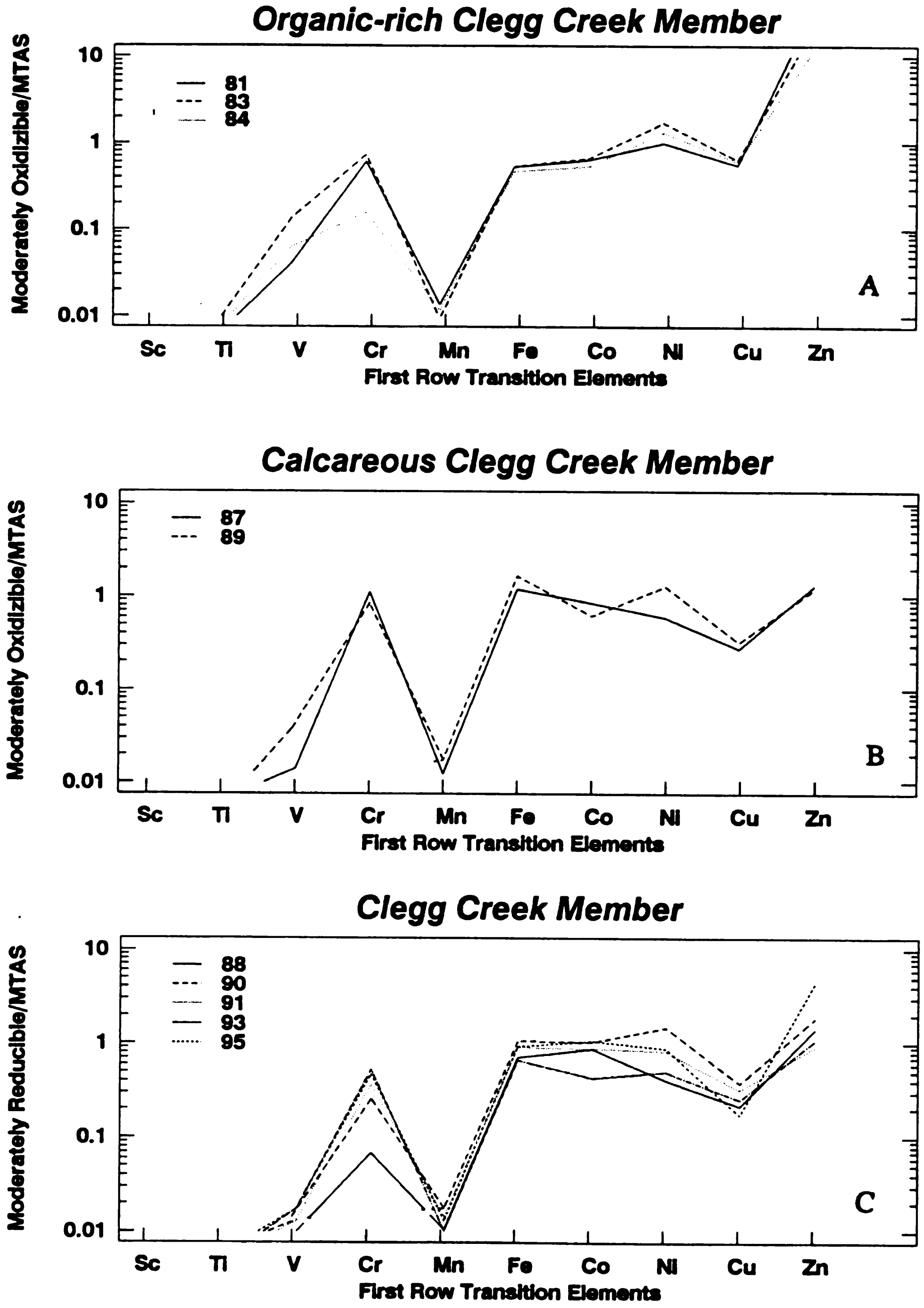
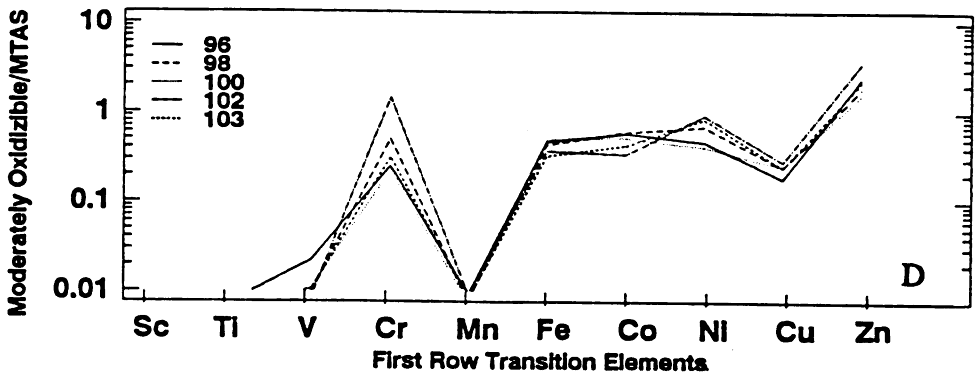
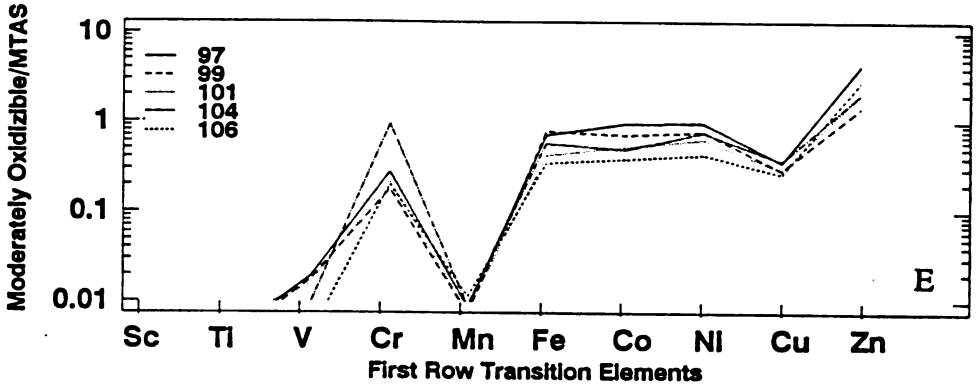


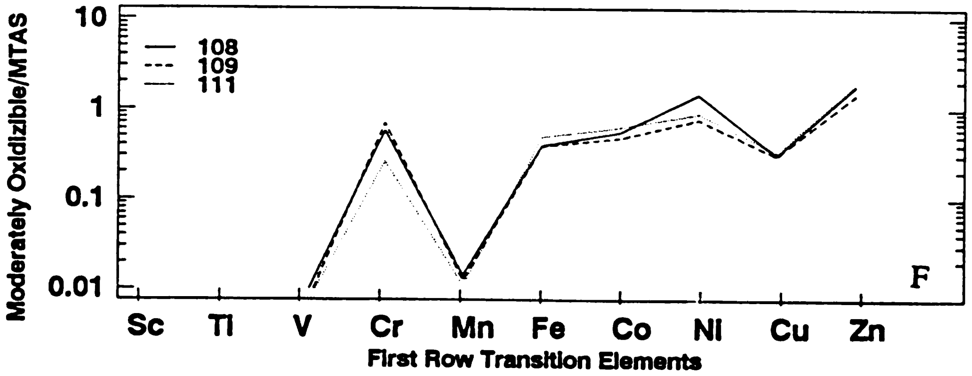
Figure 4.8. First row transition element abundances in the moderately oxidizable phase: a.) organic-rich/phosphatic, Clegg Creek Member samples; b.) calcareous, Clegg Creek Member samples; c.) black Clegg Creek samples d.) Interbedded green/black Camp Run Member samples e.) black Camp Run Member samples f.) Morgan Trail samples.



Interbedded green/black Camp Run Member



Camp Run Member



Morgan Trail Member

CONCLUSIONS

Variations in FRTE abundance patterns the untreated shale and total hydromorphic fraction are related to variations in sedimentary redox conditions, or lithologic variations among samples. Patterns for bulk and total hydromorphic samples associated with oxic sedimentary conditions are similar in shape while patterns representing anoxic conditions are highly variable. It can not be determined though analysis of bulk shale or total hydromorphic fractions which of these controls is more important in determining the FRTE distribution patterns in the shale.

The FRTE patterns for the residual fraction do not appear to be influenced by redox conditions. The pattern shows high concentrations of the lithophile elements as expected based on Goldshmidt's (1954) observations. High amounts of V and Ni in organic-rich/phosphatic Clegg Creek samples implies that insoluble organic material is contained in the residual fraction of this group. Consistent metal abundances in residual phases suggests a constant detrital source to the Illinois basin during New Albany deposition, and is in accord with the findings of Frost et al.(1985).

Variations in redox conditions can not be interpreted from isolated hydromorphic phases based on predictions made using CFT. Copper, Ni and Co are not distributed differently in sediments associated with oxidizing conditions than those representing reducing conditions. A possible explanation for these findings is that bottom water conditions may have been reducing throughout the deposition of the New Albany Shale, so that conditions were not suitable for preferential incorporation of Cu, Ni, and Co into the oxide phase.

Variations in redox conditions may be indicated by trends in the easily and moderately reducible phases. Patterns for samples associated with oxidizing conditions are relatively similar in shape while those representing reducing environment are variable in shape. The differences in pattern shapes associated with reducing conditions can not be explained in terms of redox controls and may be related to lithologic differences among samples or late diagenetic formation of secondary oxides.

The shape of the FRTE abundance pattern for total hydromorphic phase appears to be controlled by a combination of the concentrations of FRTE in all of the hydromorphic phases. Organic-rich/phosphatic and calcareous Clegg Creek Member patterns of the weakly acid soluble phase show pattern shapes similar to those of the total hydromorphic fractions. The concentrations of metals in the moderately oxidizable and weakly acid soluble phases appear to influence the total hydromorphic patterns more than other fractions in that they contain similar concentrations of FRTE. However, the pattern shapes look different for the 2 groups, because metals from several different phases contribute significantly to the total hydromorphic fraction.

Easily and moderately oxidizable phases were successfully separated using the techniques of Chou and Stanzalone (1979) and Bremmer and Lees (1945), in that each phase gave a different set of patterns. The labile organic phase appears to contain a unique trace metal signature, however more work must be done regarding the true nature of this phase. Despite possible contamination problems associated with the moderately oxidizable reaction, consistent patterns were also derived for this phase. The moderately reducible phase may be a useful new phase for use in interpreting paleochemical environments, however, more detailed experiments should be done to determine an effective way to handle the contamination problem.

Overall, the results do not firmly demonstrate that FRTE abundances record sound evidence about sedimentary redox conditions. However, Beier's (1988) initial interpretations about paleoredox conditions in the upper New Albany have recently been reassessed based on a study of organic porphyrins contained in New Albany sediments (K. Freeman, personal communication). Phytane/pristane ratios have been evaluated and indicate the presence of reducing conditions throughout New Albany deposition. This information is consistent with the results of trace metal partitioning in some of the phases examined above. To properly address the validity of the FRTE use in interpreting redox conditions, a section in which paleoredox conditions have been more thoroughly documented must be used for comparison.

APPENDICES

APPENDIX A:

ELECTROSTATIC PROPERTIES OF THE FIRST ROW TRANSITION ELEMENTS

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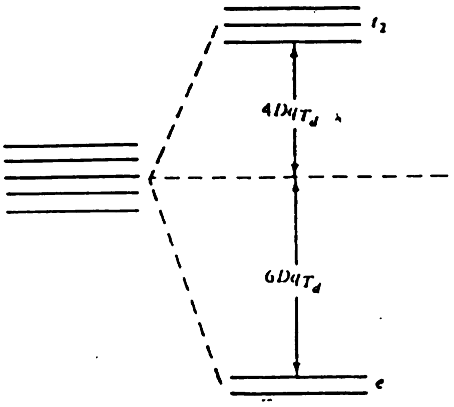
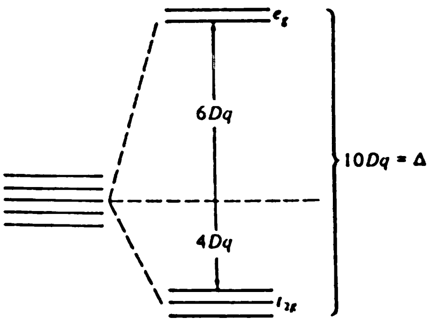
The distribution of FRTE in geologic materials is a direct consequence of each element's unique atomic structure. However, controls on the enrichment of trace elements in mineral phases are more complicated for the FRTE than for other metals. Goldshmidt's rules, based on ionic bonding assumptions, can not be used effectively to predict FRTE partitioning in that most FRTE bonds are covalent in nature (Goldschmidt, 1954). Behavior of only those FRTE whose outermost electron shells are nearly empty (Sc,Ti), or are completely filled (Zn) may be predicted using Goldschmidt's rules. Substitution of the cation which provides the largest difference in electronegativity with the surrounding anions in the crystal structure has been suggested as an alternative to Goldschmidt's rules (Ringwood, 1955); however, the opposing trends of these 2 predictive methods makes quantitative estimates on the distribution of transition elements difficult (Curtis, 1964).

Coordination chemistry provides a more accurate means of predicting FRTE behavior than do the above mentioned mechanisms in that it accounts for the electronic configuration of each element in its effects on the lattice into which it enters. Crystal field theory (CFT) provides a simple, useful, and semi-quantitative method of predicting transition element distribution in minerals (Huheey, 1983). CFT considers the energetic stability imparted to a transition element as it is transferred into a crystal lattice. The gain in energy resulting from this transfer is referred to as crystal field stabilization energy (CFSE), and is a function of the bonding affinities of the 5 d-orbitals comprising the outermost electron shell of transition elements. As the elements are moved into a mineral lattice, the five normally degenerate d-orbitals split into two distinct energy levels. Energy splitting is in response to an electrostatic field created by anions in the surrounding ligand field. As metals become incorporated into a crystal lattice they experience distortion of their orbitals which causes higher stability in some orbitals than in others. Elements with large CFSE are more favored for incorporation into minerals than are elements with low CFSE. Those FRTE having unpaired electrons are also affected by orbital distortions (called Jahn-Teller effects), which can make the metals less favorable for substitution into minerals.

The CFSE of an element is measured as the relative difference between the two energy levels resulting from d-orbital splitting, and is denoted by the value 10Dq. In a tetrahedral coordination site energy levels split as shown in Figure 2b. In an octahedral site, energy levels exhibit the configuration in Figure 2a. A list of relative 10Dq values for each of the FRTE in tetrahedral and octahedral fields is presented in Table 1. To apply CFT to real situations, Dq values for coordination sites must be known, and used to calculate CFSE from the formulas listed in Table 1. Dq values have not been determined for most mineral phases, however relative CFSEs may still be used for comparison in predicting orders of substitution into a particular mineral phase.



Splitting of *d* orbitals in a tetrahedral field.



Splitting of the degeneracy of the five *d* orbitals by an octahedral ligand field.

Figure A1. Energy level splitting of the 5-d orbitals in a.) tetrahedral and b.) octahedral coordination sites

Table A.1

Dq values for individual FRTE

Ion	No. of electrons	Stabilization in octahedral field (10Dq)	Stabilization in tetrahedral field (10Dq)
Sc^{+3}	0	0	0
Ti^{+3}	1	4	6
V^{+2}	2	8	12
Cr^{+2}	3	12	8
Mn^{+3}	4	6	4
Fe^{+3}	5	0	0
Fe^{+2}	6	4	6
Co^{+2}	7	8	12
Ni^{+2}	8	12	8
Cu^{+2}	9	6	4
Zn^{+2}	10	6	0

APPENDIX B

DETAILED LITHOLOGIC DESCRIPTIONS OF SAMPLES

APPENDIX B

DETAILED LITHOLOGIC DESCRIPTIONS OF SAMPLES

The following description copied directly from Indiana State Geological Survey preliminary core description #309:

Indiana Geological Survey Core #309

CLEGG CREEK MEMBER

Sample	Description	Depth (meters below land surface)	Thickness (meters)
81	Shale, brownish-black; phosphatic material on bedding plane (62.4); pyrite nodules (62.3, 62.5); pyrite laminae (62.4)	62.0-62.5	.5
83	Shale, brownish black; carbonate laminae (62.5-62.6); pyrite laminae (62.6)	65.2-63.0	.5
84	Shale, brownish black; carbonate laminae 64.4-64.5) pyrite nodules (64.2,64.4)	64.0-65.	1.0
86	Shale, brownish black; pyrite band (66.3, 66.6)	66.0-67.3	1.3
87	Brecciated zone; shale, brownish black to olive black, contains calcareous material and pyrite	67.3-67.6	0.3
88	Shale, brownish black	67.6-68.0	0.4
89	Brecciated zone, like unit 87	68.0-68.4	0.4
90	Shale, brownish black; some carbonate laminae; pyrite band (70.1); pyrite nodule (70.1); vitrain (68.7); Foerstia (70.1, 70.3)	68.4-70.5	2.1

91	Shale, brownish black; disseminated pyrite band (70.5, 70.7,71.1,71.4,72.4); pyrite nodule (71.4)	70.5-72.8	2.3
93	Shale, brownish black; disseminated pyrite and carbonate band (77.6, 77.8) carbonate laminae (77.4)	77.0-78.0	1.0
95	Shale, brownish black; carbonate laminae (89.5, 90.5);pyrite nodule (87.9, 88.4, 89.2, 90.2, 90.6, 90.8, 91.0)	87.0-91.1	4.1

CAMP RUN MEMBER

96	Shale, brownish black interbedded with shale, greenish gray to olive gray; pyrite nodule (91.1, 91.4, 91.7); carbonate laminae (19.2, 91.5, 91.7)	91.1-92.1	1.0
97	Shale, brownish black; shale, greenish gray to olive gray (92.7-92.9); pyrite nodule (92.1) carbonate band (92.7,92.9, 93.2); carbonate laminae (93.0)	92.1-93.8	1.7
98	Shale,brownish black interbedded with shale greenish gray to olive gray; carbonate laminae (93.8,94.2,94.8, 94.9); pyrite nodule (94.9)	93.8-96.0	2.2
99	Shale, brownish black; shale, greenish gray to olive gray (97.1-97.2); shale olive gray (96.7, 97.9-98.0, 98.4); carbonate band or laminae (96.2, 96.3, 96.6, 96.8, 97.1, 97.2, 97.4, 97.5, 97.6, 97.8, 97.9, 98.2, 98.3,98.4,98.6-98.7,98.8,98.9); pyrite nodule (97.0, 97.3, 97.9, 98.2, 98.7); pyrite band (96.8)	96.0-99.0	3.0
100	Shale, brownish black interbedded with shale, greenish gray to olive gray; abundant spores (99.5-99.6); carbonate band (99.4); pyrite nodule (99.2, 99.6); carbonate band (99.4) pyrite nodules (99.2,99.6, 99.7)	99.0-100.0	1.0

101	Shale, brownish black; shale greenish gray to olive gray (100.0-100.1, 100.7-100.8, 101.0-101.1, 102.1-102.2, 102.4-102.6); contains spores; pyrite nodule (100.2, 100.4, 100.8, 101.7,101.8); carbonate band (102.1, 102.2)	100.0-103.8	3.8
102	Shale, greenish gray to olive gray interbedded with shale, brownish black	103.8-104.9	1.1
103	Shale, brownish black; shale greenish gray to olive gray beds interbedded with brownish black beds at 106.1-106.6; brownish black shale contains spores, pyrite nodule (105.6-106.6)	104.9-106.6	1.7
104	Shale, brownish black; pyrite nodule nodule (107.4)	106.6-108.9	2.3
105	Shale, brownish black to olive black; shale olive gray to olive black (108.9-109.6); shale, olive gray (112.9-113.3); pyrite nodule (108.9,110.0, 111.1, 111.5, 111.8, 112.2, 113.8); pyrite laminae (111.8); carbonate laminae (110.0); carbonate and pyrite laminae (111.0)	108.9-114.3	5.4
106	Shale, brownish black; shale olive gray (114.3-114.5,115.0-115.2, 115.5-116.0); carbonate and pyrite laminae (115.5)	114.3-116.0	1.7

MORGAN TRAIL MEMBER

107	Shale, brownish black; shale olive gray (117.8-118.0, 118.9-119.0,119.5-119.6); pyrite nodule (117.2)	116.0-119.6	3.6
109	Shale, brownish black; pyrite nodule (128.9, 130.6); carbonate laminae (130.6)	119.6-128.7	9.1
111	Shale, brownish black to olive black; pyrite nodule (140.2, 143.1); disseminated pyrite band (140.8, 143.1, 143.5); abundant spores (141.5-141.6) disseminated pyrite and	139.5-144.2	4.7

carbonate band (142.1); shale, olive gray (143.7-143.9; carbonate laminae (144.1-144.2)

APPENDIX C

MAJOR ELEMENT CONCENTRATIONS FROM XRF DATA FOR STANDARDS ESTABLISHED USING 0.5 GRAMS OF SAMPLE (IN WEIGHT PERCENT)

APPENDIX C

MAJOR ELEMENT CONCENTRATIONS FROM XRF DATA FOR STANDARDS ESTABLISHED USING 0.5 GRAMS OF SAMPLE (IN WEIGHT PERCENT)

	STM-1*	MRG-1*	SCO-1*
SiO_2	32.73	21.96	63.74
Al_2O_3	9.967	4.697	14.09
FeO	2.973	10.58	4.404
MgO	0.004	7.632	3.813
CaO	0.678	8.544	2.654
Na_2O	4.719	0.374	0.965
K_2O	2.526	0.109	2.830
TiO_2	0.083	2.332	0.606
P_2O_5	0.094	0.042	0.223
MnO	0.142	0.107	0.056

* U.S.G.S. standard

APPENDIX D

PERCENT DISTRIBUTION OF FIRST ROW TRANSITION ELEMENTS AMONG HYDROMORPHIC AND RESIDUAL FRACTIONS

APPENDIX D

PERCENT DISTRIBUTION OF FIRST ROW TRANSITION ELEMENTS AMONG HYDROMORPHIC AND RESIDUAL FRACTIONS

TABLE 1

Titanium

SAMPLE NUMBER	WAS	ER	MR	EO	MO	RESIDUAL
81	.00	0.02	0.02	0.14	0.60	99.25
83	.00	0.02	0.02	0.15	0.83	99.00
84	.00	0.02	0.02	0.14	0.74	99.09
86	.00	1.57	1.57	19.43	79.00	0.00
87	.00	0.02	0.02	0.16	0.82	99.00
88	.00	0.01	0.01	0.16	0.81	99.03
89	.00	0.02	0.02	0.08	0.53	99.36
90	.00	0.02	0.02	0.20	1.06	98.73
91	.00	0.01	0.01	0.09	0.52	99.38
93	.00	0.01	0.01	0.18	0.70	99.11
95	.00	0.00	0.00	0.15	0.63	99.22
96	.00	0.01	0.01	0.14	0.70	99.16
97	.00	0.00	0.00	0.14	0.41	99.45
98	.00	0.01	0.01	0.17	0.38	99.44
99	.00	0.01	0.01	0.09	0.35	99.54
100	.00	0.01	0.01	0.09	0.40	99.50
101	.00	0.01	0.01	0.08	0.54	99.37
102	.00	0.01	0.01	0.17	0.38	99.45
103	.00	0.01	0.01	0.07	0.56	99.36
104	.00	0.01	0.01	0.07	0.43	99.49
106	.00	0.01	0.01	0.12	0.50	99.37
107	.00	0.01	0.01	0.11	0.62	99.27
109	.00	0.01	0.01	0.11	0.35	99.53
111	.00	0.01	0.01	0.15	0.34	99.51

WAS=weakly acid soluble, ER=weakly reducible, MR=moderately reducible, EO=easily oxidizable, MO=moderately oxidizable, RES=residual

TABLE 2

Vanadium

SAMPLE NUMBER	WAS	ER	MR	EO	MO	RESIDUAL
81	0.01	0.05	0.54	0.10	0.20	99.10
83	0.05	0.30	1.16	0.11	0.63	97.74
84	0.08	0.25	0.74	0.09	0.32	98.53
86	1.33	3.54	65.85	6.50	22.78	0.00
87	0.06	0.04	0.41	0.02	0.09	99.37
88	0.00	0.02	0.28	0.06	0.09	99.54
89	0.00	0.03	0.36	0.02	0.08	99.52
90	0.02	0.05	0.35	0.03	0.11	99.44
91	0.02	0.05	0.20	0.01	0.07	99.66
93	0.00	0.02	0.23	0.04	0.12	99.58
95	0.02	0.05	0.28	0.02	0.09	99.54
96	0.01	0.03	0.30	0.03	0.10	99.53
97	0.03	0.04	0.26	0.03	0.09	99.55
98	0.03	0.04	0.28	0.06	0.05	99.55
99	0.01	0.04	0.22	0.02	0.08	99.64
100	0.01	0.02	0.23	0.02	0.05	99.67
101	0.01	0.04	0.22	0.01	0.07	99.65
102	0.01	0.02	0.20	0.02	0.04	99.70
103	0.01	0.03	0.25	0.01	0.05	99.65
104	0.02	0.02	0.23	0.01	0.05	99.68
106	0.01	0.02	0.21	0.03	0.02	99.71
107	0.02	0.03	0.23	0.02	0.05	99.66
109	0.01	0.05	0.27	0.02	0.03	99.62
111	0.02	0.04	0.29	0.02	0.04	99.60

WAS=weakly acid soluble, ER=weakly reducible, MR=moderately reducible, EO=easily oxidizable, MO=moderately oxidizable, RES=residual

TABLE 3

Chromium

SAMPLE NUMBER	WAS	ER	MR	EO	MO	RESIDUAL
81	0.13	0.01	12.27	0.32	23.14	64.14
83	0.11	0.01	24.11	0.21	22.10	53.46
84	0.21	0.01	14.10	0.33	8.59	76.76
87	0.21	0.01	27.28	0.14	46.09	26.27
88	0.24	0.00	42.34	0.45	6.37	50.59
89	0.24	0.01	40.45	0.17	27.70	32.34
90	0.35	0.02	20.35	0.44	36.02	42.81
91	0.32	0.03	17.35	0.29	29.39	52.62
93	0.13	0.01	31.87	0.39	32.67	34.93
95	0.41	0.03	22.31	0.33	29.69	47.22
96	0.26	0.03	35.55	0.53	15.37	48.26
97	0.39	0.04	27.45	0.54	19.01	52.57
98	0.34	0.02	28.27	0.70	26.57	44.11
99	0.34	0.03	26.72	0.37	13.06	59.48
100	0.28	0.02	32.95	0.34	13.44	52.97
101	0.35	0.04	29.40	0.25	13.58	56.38
102	0.29	0.02	19.01	0.34	49.56	30.78
103	0.28	0.03	31.04	0.32	17.56	50.77
104	0.19	0.01	19.45	0.21	40.69	39.45
106	0.33	0.03	31.92	0.59	11.69	55.44
107	0.20	0.02	25.23	0.34	28.48	45.72
109	0.21	0.02	21.23	0.32	34.89	43.35
111	0.34	0.02	23.70	0.48	18.75	56.71

WAS=weakly acid soluble, ER=weakly reducible, MR=moderately reducible, EO=easily oxidizable, MO=moderately oxidizable, RES=residual

TABLE 4

Manganese

SAMPLE NUMBER	WAS	ER	MR	EO	MO	RESIDUAL
81	2.96	1.27	71.50	3.75	1.16	19.36
83	8.11	5.04	15.90	2.99	2.61	65.35
84	4.08	2.86	61.28	2.76	1.37	27.64
86	3.96	0.40	69.19	2.49	0.97	22.99
87	16.17	5.30	69.76	1.52	0.35	6.90
88	5.46	1.57	62.83	2.94	1.09	26.11
89	10.29	7.06	73.70	0.86	0.52	7.57
90	17.69	12.46	25.53	2.11	2.75	39.48
91	40.25	12.59	15.40	0.77	1.62	29.37
93	23.05	4.74	16.43	2.54	1.98	51.27
95	17.69	25.10	31.65	1.77	1.09	22.71
96	12.23	8.43	64.46	1.79	0.43	12.65
97	20.02	16.34	41.19	2.00	0.62	19.82
98	22.37	12.48	50.57	2.80	0.56	11.80
99	9.87	19.90	40.88	2.41	0.68	26.26
100	14.04	7.68	59.77	2.19	0.42	15.90
101	24.01	10.68	44.56	2.28	0.49	17.99
102	11.48	9.50	55.53	2.65	0.65	20.19
103	13.04	12.32	46.59	2.46	0.70	24.88
104	11.37	9.07	56.47	2.92	0.59	19.58
106	7.96	9.91	50.93	3.32	1.03	26.86
107	10.08	12.30	50.38	2.61	1.11	23.51
109	13.22	16.27	39.21	2.47	1.12	27.71
111	12.66	14.69	36.34	2.47	1.14	32.69

WAS=weakly acid soluble, ER=weakly reducible, MR=moderately reducible, EO=easily oxidizable, MO=moderately oxidizable, RES=residual

TABLE 5

Iron

SAMPLE NUMBER	WAS	ER	MR	EO	MO	RESIDUAL
81	0.22	0.56	8.98	0.49	29.20	60.55
83	0.23	0.88	5.66	0.45	39.11	53.67
84	0.35	0.72	7.41	0.33	32.94	58.24
86	0.35	0.35	9.07	0.33	36.94	52.95
87	2.75	1.28	12.25	0.44	30.54	52.74
88	0.21	0.60	11.05	0.35	29.16	58.64
89	1.09	0.77	8.22	0.28	29.59	60.06
90	0.53	0.83	2.97	0.22	43.62	51.83
91	0.75	1.44	3.00	0.17	36.43	58.20
93	0.22	0.78	13.87	0.60	27.03	57.49
95	0.55	0.99	6.40	0.32	37.46	54.27
96	1.19	0.90	17.21	0.69	22.17	57.84
97	1.02	1.13	10.64	0.38	32.44	54.38
98	1.94	2.00	13.00	0.41	26.87	40.68
99	0.72	1.13	8.80	0.31	31.15	57.88
100	1.33	0.82	15.19	0.71	25.19	56.75
101	0.80	1.08	33.06	0.55	17.10	47.41
102	1.24	1.35	18.80	0.80	20.57	57.24
103	0.80	1.19	19.08	0.78	18.40	59.74
104	0.59	0.56	12.55	0.56	27.08	58.66
106	0.77	1.04	19.48	1.02	19.48	58.21
107	0.75	1.13	13.88	0.73	23.00	60.51
109	0.90	1.27	16.01	0.55	22.44	58.83
111	0.84	0.77	12.18	0.43	29.23	56.55

WAS=weakly acid soluble, ER=weakly reducible, MR=moderately reducible, EO=easily oxidizable, MO=moderately oxidizable, RES=residual

TABLE 6

Cobalt

SAMPLE NUMBER	WAS	ER	MR	EO	MO	RESIDUAL
81	14.80	1.21	19.26	0.88	28.18	35.67
83	12.12	3.36	13.10	0.96	70.43	0.05
84	13.20	3.41	15.90	0.50	66.94	0.06
87	16.29	2.04	24.71	1.74	52.06	3.17
88	5.95	1.39	17.41	0.97	65.28	9.00
89	8.19	0.95	15.26	2.68	30.73	42.18
90	9.49	2.81	19.01	1.40	61.91	5.38
91	9.89	2.97	16.95	1.26	54.69	14.24
93	5.87	1.26	34.61	1.44	43.76	13.06
95	10.36	4.45	15.59	1.68	57.08	10.84
96	18.94	4.29	27.03	2.75	46.95	0.03
97	8.11	2.24	10.37	0.72	42.55	36.02
98	12.52	4.50	17.28	2.08	33.56	30.05
99	7.85	3.84	13.80	1.19	30.77	42.55
100	11.66	2.61	17.89	1.54	23.13	43.16
101	13.75	5.89	25.50	1.44	35.26	18.15
102	14.96	5.82	27.12	1.84	27.81	22.45
103	11.86	5.56	25.52	1.45	32.12	23.49
104	9.32	3.19	19.55	1.41	30.16	36.37
106	12.97	7.49	23.73	2.14	37.17	16.50
107	9.82	6.25	20.11	2.14	48.97	12.71
109	7.94	4.32	19.98	1.51	43.00	23.24
111	12.12	2.79	20.36	2.07	50.56	12.10

WAS=weakly acid soluble, ER=weakly reducible, MR=moderately reducible, EO=easily oxidizable, MO=moderately oxidizable, RES=residual

TABLE 7

Nickel

SAMPLE NUMBER	WAS	ER	MR	OR	MO	RESIDUAL
81	2.06	0.35	4.03	0.37	18.54	74.65
83	4.31	1.10	5.27	0.33	42.91	46.07
84	3.18	1.05	4.50	0.28	45.78	45.20
86	3.05	3.47	6.11	0.39	86.98	0.00
87	5.94	1.07	9.71	1.01	47.96	34.31
88	3.89	0.63	8.05	0.50	46.98	39.93
89	1.86	0.51	5.73	0.71	76.34	14.84
90	2.48	1.40	7.56	0.44	73.46	14.66
91	3.64	2.09	8.56	0.57	56.34	28.80
93	2.70	0.65	9.88	0.42	44.62	41.72
95	5.10	2.43	11.99	1.44	47.06	31.98
96	7.59	2.39	14.66	2.09	34.74	38.53
97	4.96	1.72	8.59	0.95	50.94	32.83
98	4.19	2.42	9.89	2.40	45.11	35.99
99	4.08	2.63	11.65	1.23	48.79	31.63
100	7.41	2.30	15.62	1.97	35.49	37.20
101	4.33	2.22	10.84	1.16	45.65	35.80
102	2.91	1.53	8.03	0.69	60.76	26.08
103	3.11	1.93	9.93	0.46	53.60	30.95
104	3.11	1.54	11.07	0.61	49.70	33.98
106	3.53	2.54	11.66	0.74	43.83	37.69
107	1.49	1.32	5.31	0.52	69.92	21.45
109	2.18	1.98	10.65	0.67	55.68	28.84
111	4.11	1.69	10.20	1.09	56.65	26.27

WAS=weakly acid soluble, ER=weakly reducible, MR=moderately reducible, EO=easily oxidizable, MO=moderately oxidizable, RES=residual

TABLE 8

Copper

SAMPLE NUMBER	WAS	ER	MR	EO	MO	RESIDUAL
81	12.05	1.05	2.81	11.07	60.96	12.07
83	3.74	0.20	14.71	3.10	70.35	7.89
84	2.47	0.01	2.64	6.15	88.55	0.18
87	1.39	0.00	6.97	12.28	79.05	0.31
88	10.43	0.77	8.11	18.50	51.63	10.55
89	0.92	0.07	8.24	9.69	80.81	0.27
90	0.53	0.00	6.04	11.24	82.02	0.17
91	0.14	0.00	0.94	10.31	84.37	4.24
93	6.55	1.67	7.04	45.02	34.35	5.36
95	1.24	0.00	6.83	62.13	29.63	0.18
96	1.47	0.14	9.52	52.04	36.61	0.22
97	0.53	0.00	8.69	14.29	76.27	0.23
98	0.51	0.09	7.69	40.10	51.39	0.22
99	3.55	0.00	6.03	42.11	42.63	5.68
100	1.07	0.12	10.01	45.54	43.26	0.00
101	5.13	0.01	3.42	40.69	45.72	5.02
102	4.61	0.06	13.83	14.18	67.07	0.25
103	7.10	0.03	11.07	16.49	56.63	8.68
104	2.76	0.32	6.38	36.60	51.47	2.48
106	4.64	0.12	14.55	13.47	66.96	0.27
107	2.31	0.00	7.23	16.22	73.98	0.25
109	5.31	0.00	7.37	13.58	73.47	0.27
111	2.40	0.12	8.10	46.54	41.36	1.49

WAS=weakly acid soluble, ER=weakly reducible, MR=moderately reducible, EO=easily oxidizable, MO=moderately oxidizable, RES=residual

TABLE 9

Zinc

SAMPLE NUMBER	WAS	ER	MR	EO	MO	RESIDUAL
81	2.59	1.05	14.05	2.16	75.42	4.72
83	3.99	2.59	20.36	2.43	67.93	2.69
84	0.12	2.04	24.79	3.06	68.66	1.32
87	1.53	0.64	8.79	4.14	79.24	5.67
88	3.32	1.72	7.56	9.62	71.96	5.81
89	1.65	0.42	5.79	0.68	87.84	3.62
90	1.26	0.23	6.99	2.81	84.73	3.98
91	1.75	0.00	11.76	1.65	73.85	10.99
93	13.33	2.35	11.76	3.92	59.43	9.20
95	0.73	1.07	11.90	3.44	81.11	1.76
96	1.55	1.89	17.02	4.95	67.99	6.60
97	1.37	1.32	18.24	3.16	74.09	1.83
99	4.14	2.73	11.34	4.42	71.50	5.87
100	2.95	1.16	7.41	2.49	80.91	5.09
101	3.00	1.28	7.02	3.51	80.94	4.25
102	0.38	0.94	4.28	1.83	89.98	2.60
103	11.81	2.49	14.61	2.27	65.10	3.72
104	6.75	0.80	7.19	2.53	78.13	4.59
106	3.94	0.32	5.98	2.34	84.20	3.22
107	7.04	1.79	6.32	2.78	76.81	5.26
109	6.22	1.67	10.22	6.22	68.51	7.17
111	6.37	1.30	7.71	3.86	77.13	3.63

WAS=weakly acid soluble, ER=weakly reducible, MR=moderately reducible, EO=easily oxidizable, MO=moderately oxidizable, RES=residual

APPENDIX E

FIRST ROW TRANSITION ELEMENT CONCENTRATIONS IN UNTREATED SHALE AND CHEMICALLY SEPARABLE FRACTIONS

APPENDIX E

FIRST ROW TRANSITION ELEMENT CONCENTRATIONS IN UNTREATED SHALE AND CHEMICALLY SEPARABLE FRACTIONS

TABLE 1

First row transition element concentrations in bulk shale samples (ppm)

Sample number	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
81	3886.8	671.07	175.6	428.4	39631.7	71.05	581.5	124.6	3753.2
83	3132.0	997.45	183.8	93.0	26786.7	23.67	357.2	137.5	3250.2
84	3468.0	680.73	146.3	263.4	29670.7	21.85	236.1	111.5	1892.4
86	3152.4	201.42	75.5	440.0	58480.3	48.26	128.0	65.6	33.9
87	2263.8	135.49	50.3	1193.0	74921.0	56.35	91.6	46.5	24.8
88	3369.6	170.06	70.4	362.5	51809.3	77.70	88.9	58.2	28.4
89	1776.0	100.59	40.1	1177.5	122080.0	56.94	39.7	34.4	16.1
90	2769.0	186.51	69.4	201.4	45803.3	50.92	100.5	56.0	36.5
91	2897.9	179.07	67.2	241.4	52227.6	49.16	98.3	61.1	32.2
93	2980.8	159.51	59.5	223.1	51408.0	45.69	113.3	65.6	51.5
95	3804.6	214.44	79.4	404.5	49376.9	46.99	146.4	80.8	408.5
96	4362.5	196.18	84.2	746.4	44150.4	39.42	98.4	55.9	286.8
97	4437.6	228.13	89.0	466.3	43477.8	35.11	146.1	74.7	458.9
98	4352.5	222.93	94.3	609.3	38135.5	31.36	111.7	59.0	330.9
99	4183.2	203.43	87.0	385.8	53129.2	39.07	115.9	85.4	109.8
100	4247.9	196.92	95.0	528.6	40735.5	29.58	88.2	62.5	54.9
101	4485.6	197.35	91.8	482.6	42156.3	28.88	96.6	81.2	79.6
102	4664.6	183.37	92.8	490.2	36843.0	23.97	69.3	56.5	185.6
104	4360.5	186.35	98.6	331.2	35752.5	24.37	96.8	80.0	202.8
106	4176.0	200.90	96.7	539.2	45133.7	27.65	94.3	84.8	67.6
107	4394.5	193.29	107.4	363.7	37758.2	18.91	79.6	60.8	159.6
109	3990.2	199.67	104.0	423.4	37270.0	20.29	82.0	75.3	55.6
111	3549.0	166.73	89.8	3679.0	36804.4	21.01	83.9	80.7	117.1

TABLE 2

Transition element concentrations in weakly acid soluble phase (mg/l)

Sample number	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
81	0.00	0.22	0.31	12.1	144	7.5	9.6	9.0	141.0
83	0.00	2.20	0.34	10.3	116	2.6	14.7	2.8	96.0
84	0.00	2.93	0.36	12.4	180	2.4	7.9	1.4	120.0
86	0.00	0.24	0.43	14.8	392	2.2	4.9	2.5	2.3
87	0.00	1.75	0.47	204.0	3912	6.0	6.3	0.4	3.3
88	0.00	0.04	0.24	18.4	184	1.8	2.9	3.6	2.4
89	0.00	0.04	0.36	121.0	2224	3.7	2.7	.3	3.8
90	0.00	0.50	0.36	40.3	470	3.6	4.3	0.2	3.9
91	0.00	0.75	0.37	124.7	676	3.6	4.6	0.0	2.6
93	0.00	0.04	0.20	41.8	200	1.3	2.6	4.0	1.9
95	0.00	0.64	0.61	74.0	500	4.4	8.3	0.6	17.0
96	0.00	0.62	0.38	92.8	912	5.2	8.8	0.6	1.6
97	0.00	1.16	0.52	98.0	816	4.1	8.2	0.2	38.0
98	0.00	1.16	0.58	106.0	739	5.0	5.5	0.2	16.8
99	0.00	0.21	0.44	37.2	660	4.1	5.6	2.0	4.1
100	0.00	0.49	0.42	88.3	956	5.8	7.4	0.5	4.1
101	0.00	0.30	0.51	134.8	708	4.6	5.2	2.7	7.3
102	0.00	0.57	0.78	58.0	800	4.1	3.8	1.6	12.3
103	0.00	0.27	0.47	54.0	504	3.5	4.1	2.5	15.7
104	0.00	0.61	0.41	60.4	456	3.4	4.1	1.6	7.6
106	0.00	0.55	0.52	31.4	500	3.0	3.0	1.5	11.2
107	0.00	0.59	0.37	45.9	464	2.5	2.7	0.8	5.1
109	0.00	0.23	0.39	52.0	560	2.0	2.6	1.8	7.0
111	0.00	0.55	0.44	43.0	520	3.4	5.6	1.6	14.7

TABLE 3

Transition element concentrations in the easily reducible fraction (mg/l)

Sample number	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
81	0.03	2.17	0.013	5.3	366	0.61	1.64	0.78	39.2
83	0.00	12.10	0.025	6.4	439	0.72	3.75	0.15	78.3
84	0.00	9.24	0.011	8.7	366	0.62	2.61	0.01	38.4
86	0.00	0.64	0.027	1.5	390	0.28	5.56	0.30	1.6
87	0.00	1.32	0.016	66.8	1819	0.75	1.14	0.00	1.4
88	0.00	0.40	0.002	5.3	526	0.42	0.47	0.27	3.5
89	0.04	0.70	0.012	83.0	1560	0.43	0.74	0.02	1.1
90	0.00	1.14	0.017	28.4	734	1.07	2.42	0.00	0.1
91	0.01	1.68	0.031	39.0	1291	1.08	2.64	0.00	0.0
93	0.01	0.54	0.009	8.6	695	0.28	0.62	1.02	3.3
95	0.00	1.80	0.049	105.0	902	1.89	3.95	0.00	6.2
96	0.00	1.34	0.041	64.0	687	1.18	2.77	0.06	5.5
97	0.04	1.73	0.054	80.0	902	1.13	2.84	0.00	7.3
98	0.02	1.67	0.032	59.0	757	1.85	3.18	0.03	6.2
99	0.01	1.44	0.042	75.0	1035	2.01	3.61	0.00	5.1
100	0.01	1.00	0.036	48.3	591	1.30	2.30	0.06	2.0
101	0.00	1.78	0.066	60.0	963	1.97	2.67	0.01	3.4
102	0.00	1.12	0.055	48.0	867	1.60	2.00	0.02	4.5
103	0.04	1.46	0.045	51.0	748	1.64	2.61	0.01	8.2
104	0.01	0.70	0.021	48.2	432	1.16	2.04	0.19	2.3
106	0.00	0.80	0.043	39.1	675	1.73	2.16	0.04	1.4
107	0.00	1.07	0.038	56.0	696	1.59	2.38	0.00	4.1
109	0.00	1.62	0.032	64.0	795	1.09	2.36	0.00	3.3
111	0.01	1.32	0.023	49.9	471	0.78	2.30	0.08	3.2

TABLE 4

Transition element concentrations in the moderately reducible fraction (mg/l)

Sample number	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
81	0.79	21.60	30.1	299.1	5878.0	9.76	18.8	2.1	520.0
83	0.65	47.04	74.0	20.2	2827.2	2.81	18.0	11.0	612.0
84	0.91	27.84	24.0	186.2	3777.1	2.89	11.2	1.5	461.0
86	0.46	11.88	45.4	258.8	10020.1	5.92	9.8	1.7	14.2
87	0.57	12.19	61.0	880.0	17400.3	9.10	10.3	2.0	13.8
88	0.16	5.80	42.3	211.8	9766.6	5.27	6.0	2.8	13.2
89	0.55	8.08	60.9	866.8	16700.5	6.89	8.3	2.7	13.7
90	0.37	8.07	20.9	58.2	2626.4	7.21	13.1	2.3	14.4
91	0.24	7.32	20.3	47.7	2689.3	6.17	10.8	0.3	12.8
93	0.22	6.33	48.0	29.8	12400.1	7.67	9.5	4.3	15.0
95	0.18	10.47	33.0	132.4	5826.1	6.62	19.5	3.3	67.0
96	0.24	12.81	52.9	489.1	13137.3	7.42	17.0	3.9	45.0
97	0.19	10.65	37.0	201.6	8510.6	5.24	14.2	3.3	97.0
98	0.34	11.61	49.1	240.0	10100.6	6.23	13.0	3.0	18.4
99	0.28	8.76	34.1	154.1	8082.5	7.21	16.0	3.4	20.8
100	0.25	9.79	50.0	375.9	10900.4	8.90	15.6	4.7	12.8
101	0.24	9.35	43.7	250.2	10928.3	8.53	13.0	1.8	16.4
102	0.28	9.18	51.1	280.6	12100.1	7.43	10.5	4.8	18.2
103	0.31	11.27	50.9	192.9	12000.2	7.53	13.4	3.9	47.0
104	0.37	8.94	41.9	300.0	9653.1	7.13	14.6	3.7	17.9
106	0.32	8.11	50.7	201.0	12639.1	5.49	9.9	4.7	18.7
107	0.28	8.33	47.0	229.3	8552.5	5.12	9.6	2.5	14.1
109	0.36	9.46	39.8	154.2	10018.3	5.03	12.7	2.5	18.4
111	0.269	9.73	31.1	123.4	10100.2	5.71	13.9	5.4	17.8

TABLE 5

Transition element concentrations in the easily oxidizable fraction (mg/l)

Sample number	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
81	5.44	3.89	0.78	15.7	320.0	0.45	1.74	8.27	80.0
83	5.96	4.60	0.66	3.8	223.0	0.20	1.14	2.32	73.0
84	5.22	3.28	0.57	8.4	168.0	0.09	0.70	3.49	57.0
86	5.66	1.17	0.48	9.3	367.0	0.20	0.62	30.10	5.1
87	4.82	0.69	0.30	19.2	631.8	0.64	1.08	3.52	6.5
88	3.26	1.31	0.45	9.9	310.0	0.29	0.38	6.38	16.8
89	1.72	0.38	0.25	10.1	559.8	1.21	1.04	3.18	1.6
90	4.50	0.65	0.46	4.8	190.0	0.53	0.76	4.28	5.8
91	3.44	0.45	0.34	2.4	157.0	0.46	0.72	3.28	1.8
93	4.96	1.09	0.59	4.6	540.0	0.32	0.41	27.49	5.0
95	5.60	0.82	0.49	7.4	293.0	0.72	2.34	30.04	19.4
96	5.92	1.50	0.79	13.6	527.4	0.76	2.41	21.31	13.1
97	5.60	1.31	0.72	9.8	306.0	0.37	1.58	5.43	16.8
98	7.20	2.40	1.22	13.3	495.0	0.83	3.15	15.64	18.2
99	3.84	0.76	0.47	9.1	288.0	0.62	1.69	23.75	8.1
100	3.84	0.75	0.52	13.8	513.0	0.77	1.97	21.37	4.3
101	3.52	0.50	0.37	12.8	486.0	0.48	1.39	21.40	8.2
102	7.52	1.08	0.91	13.4	513.0	0.50	0.90	4.92	7.8
103	3.20	0.63	0.53	10.2	493.2	0.43	0.63	5.81	7.3
104	2.88	0.40	0.44	15.5	432.0	0.51	0.80	21.23	6.3
106	4.48	1.06	0.94	13.1	658.8	0.50	0.63	4.35	7.3
107	4.00	0.71	0.64	11.9	448.2	0.55	0.94	5.60	6.2
109	3.84	0.72	0.59	9.7	344.0	0.38	0.80	4.60	11.2
111	4.96	0.79	0.63	8.4	266.0	0.58	1.48	31.02	8.9

TABLE 6

Transition element concentrations in the moderately oxidizable fraction (mg/l)

Sample number	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
81	23.71	7.82	56.77	4.84	19111.1	14.28	86.53	45.55	3678.2
83	33.52	25.79	67.85	3.32	19519.3	15.11	146.51	52.60	2130.3
84	27.69	11.92	14.62	4.17	16783.2	12.17	113.84	50.22	1208.3
86	23.02	4.11	83.85	3.64	40799.4	18.28	139.52	28.38	123.1
87	24.39	2.69	103.06	4.38	43384.5	19.18	50.88	22.68	141.0
88	16.61	1.88	6.36	3.68	25760.2	19.76	35.00	17.82	152.7
89	12.14	1.73	42.00	6.15	60141.4	13.88	110.64	26.48	128.4
90	24.46	2.53	34.7	6.26	38546.5	23.49	127.32	31.22	198.0
91	19.38	2.46	34.39	5.02	32692.2	19.91	71.12	26.83	98.1
93	19.15	3.33	49.20	3.58	24172.3	9.70	42.92	20.98	116.5
95	23.26	3.33	43.91	4.57	34085.1	24.24	76.56	14.32	475.2
96	30.13	4.20	22.88	3.27	16920.3	12.89	40.29	14.99	253.6
97	16.95	3.60	25.63	3.06	25937.2	21.51	84.20	28.98	459.1
98	15.79	1.91	46.14	2.74	15474.1	13.42	59.28	20.04	195.2
99	14.43	3.37	16.66	2.55	28597.3	16.07	67.00	24.04	155.2
100	17.30	2.05	20.39	2.63	18081.5	11.51	35.44	20.31	165.3
101	23.30	2.98	20.18	2.74	15208.3	11.79	54.76	24.04	219.3
102	17.17	1.62	133.20	3.29	13238.1	7.62	79.44	23.28	374.1
103	24.95	2.00	28.80	2.90	11573.3	9.48	72.32	19.95	233.4
104	17.13	1.87	87.64	3.16	20838.2	11.00	65.56	29.86	220.5
106	19.55	0.81	18.57	4.06	12639.3	8.60	37.20	21.63	301.7
107	22.47	1.64	53.06	5.04	14164.5	12.47	126.48	25.57	196.2
109	11.97	1.21	65.40	4.40	14041.6	10.83	66.40	24.91	156.5
111	11.41	1.23	24.61	3.88	17989.1	14.18	77.24	27.57	200.3

TABLE 7

Transition element concentrations in the residual fraction (mg/l)

Sample number	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
81	3950.3	624.14	157.36	66.18	15109.4	18.08	348.38	9.02	174.84
83	3973.2	916.56	164.10	84.41	17859.3	0.01	157.30	5.90	80.90
84	3695.3	726.99	130.70	53.61	10818.3	0.01	112.40	0.10	24.50
86	2956.8	155.43	58.74	54.53	11936.5	1.17	36.40	0.09	8.90
88	2042.9	137.15	50.54	34.70	11289.6	2.72	29.75	3.64	10.15
89	2261.0	122.39	48.87	55.07	52811.5	19.04	21.51	0.09	8.55
90	2276.4	132.89	43.97	37.68	8247.2	2.04	25.41	0.06	8.19
91	3685.5	161.85	61.56	63.44	17836.0	5.18	36.36	1.35	11.97
93	2707.1	164.69	52.60	52.16	10265.6	2.89	40.13	3.28	11.74
95	3676.5	193.93	69.83	49.97	9331.0	4.60	52.03	0.09	9.89
96	4296.8	182.30	71.82	58.40	10612.3	0.01	44.68	0.09	17.44
97	4111.5	186.48	70.86	55.29	8161.1	18.20	54.27	0.09	9.72
98	4117.7	168.25	76.61	55.96	10226.0	12.01	47.29	0.08	15.46
99	4045.8	175.02	75.92	31.85	14841.0	22.22	43.43	3.20	10.77
100	4249.9	163.34	80.39	57.76	9916.4	21.47	37.15	0.00	8.79
101	4259.9	166.34	83.81	58.51	11572.9	6.07	42.95	2.64	9.91
102	4516.6	150.54	82.74	60.12	10502.4	6.15	34.10	0.09	11.05
103	4416.1	165.02	83.25	41.55	11632.0	6.93	41.76	3.06	11.97
104	3955.3	159.76	84.96	57.38	12789.4	13.27	44.82	1.44	11.43
106	3855.1	150.42	88.06	56.56	9143.0	3.82	32.00	0.09	10.06
107	3623.6	160.10	85.17	57.76	11540.1	3.24	38.80	0.09	11.74
109	3447.7	164.46	81.26	61.82	11359.2	5.85	34.40	0.09	12.92
111	3358.6	159.10	74.43	59.40	9959.9	3.39	35.82	0.99	8.37

LIST OF REFERENCES

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