Geochemical relationships of Late Paleozoic carbon-rich shales of the Midcontinent, USA: a compendium of results advocating changeable geochemical conditions

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Abstract

Previous studies have shown that Pennsylvanian black shales of the Midcontinent US possess a more complex geochemical history than was once thought. Vine and Tourtelot [Econ. Geol. 65 (1970) 253] and Coveney and Glascock [Appl. Geochem. 4 (1989) 347] note that the widespread nature of metalliferous Pennsylvanian black shales and the diverse geological environments across the Midwestern US pose the likelihood that metals contained in the black shales are of complex origins. Detailed geochemical and statistical representations using characteristics of numerous black shale members have shown that water depth may not have been uniformly "deep" as previously inferred by numerous workers. Earlier suggestions that these black shales were associated exclusively with anoxic depositional conditions have been challenged by a more realistic theory of multifaceted, fluctuating environmental conditions.

A wide range of major and trace element concentrations, combined with widely varying characteristics and diverse types of organic matter, indicate the presence of fluctuating geochemical settings. The presumption is that numerous associated chemical reactions occurred syngenetically. One geochemical index, degree of pyritization (DOP), suggests a dysaerobic to aerobic setting for many of the shales, whereas some other geochemical proxies (i.e., $V/(V+Ni)$) indicate punctuated episodes of bottom water anoxia. Schieber [Abstr. Programs-Geol. Soc. Am. 33/6 (2001) A102] notes that in some black shales, pyrite enrichment due to intermittent organic reworking explains the high DOP values, once thought to equate with extreme euxinic depositional conditions. It seems likely, therefore, that even during apparent euxinic periods as indicated by bulk geochemistry, oxygen-deprived events were apparently shortlived. The seemingly euxinic "fingerprint" as shown by geochemical characteristics, may result through "time averaging" [Abstr. Programs-Geol. Soc. Am. 33/6 (2001) A102] of intermittent euxinic "events", providing a misleading indication of dominant euxinic conditions. Thus, detailed microstratigraphic sampling is necessary to delineate short, punctuated occurrences of intermittent sub-oxic episodes. The Midcontinent Pennsylvanian shales may reflect a complex array of bottom water oxygenation variations and water depth fluctuations in response to climatic and localized events [Hatch, J.R., and Leventhal, J.S., (1992). Relationship between inferred redox potential of the depositional environment and geochemistry of the Upper Pennsylvanian (Missourian) Stark Shale Member of the Dennis Limestone, Wabaunsee County, Kansas, USA. In: Meyers, P.A., Pratt, L.M., Nagy, B. (Eds.), Geochemistry of Metalliferous Black Shales. Chem. Geol. 99, 65–82.], complicated by post-depositional events [Appl. Geochem. 4 (1989) 347]. This research examines the previous "exclusively anoxic" origin for Midcontinent Pennsylvanian black shales from a geochemical perspective and offers an

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alternative supported by detailed statistical presentations with the hypothesis that events of anoxia were punctuated by short-lived dysaerobic or even near-oxic events.

1. Introduction

The study of black shales has been challenging until the last few decades. Early work was hampered because outcrops, however accessible, yielded only limited data about the genesis of black shales, and weathering potentially obscured the diagenetic activities. Generally, theories of their origin were limited to the simple explanation that black shales were formed in relatively deep water and under reducing conditions. Significant early work on black shales addressed the importance of anoxia and their formation (Pettijohn, 1949), association with a distinctive biofacies (Bulman, 1955), and the conclusion that, under modern conditions, these facies were formed in basins restricted from free exchange with the open ocean, leading to stagnation in the bottom portion of the water column (Strom, 1939). Such settings are relatively unusual in occurrence today, but portions of the Lower Paleozoic and Mesozoic rock records are indicative of a generally more widespread anoxia when global climates were warmer and more surficially hospitable.

The chemistry of black shales has generally attracted scientific attention, but only until fairly recently have new technological advancements propelled geochemical studies to a point where new hypotheses could be tested. Geochemistry has played a major role in the characterization of both organic material and inorganic constituents, widening the scope of inferences drawn about the genesis of black shales. Considerable progress has been made in understanding the geochemistry of black shales by going beyond traditional bulk analyses, placing an emphasis on deciphering the speciation of the elements. Ore microscopy has been instrumental in determining metal speciation. The matter of speciation on metals relies on a few selected indirect methods and does not refer to the direct evidence of speciation covered by ore microscopy (Coveney, 1979, personal communication). Particularly germane to the studies are the behavior of metals and the determination of the oxidation state of S, since

many heavy metals are immobilized in the presence of sulfide (Canfield et al., 1986) as can been seen by ore microscopy (Coveney, personal communication; Ripley, written communication). Raiswell and Berner (1985) combined the determination of S species with similar Fe measurements into a parameter referred to as degree of pyritization (DOP), originally defined by Berner (1970) as:

$$DOP = \text{Pyritic iron } (Fe_{py})/(Fe_{py} + HCl\text{-soluble iron}(Fe_{HCl}))$$

DOP, combined with various ratios including C/S, has been used in the past to successfully quantify the degree of anoxia (DOA). However, it must be noted, C/S ratios in these settings are also vulnerable to weathering during sea-level lowstands and must be used with caution (Lyons et al., 2002). More recent work by workers (Hoffman et al., 1998) has shown that the combination of faunal, ichnofabric, and geochemical data have proven effective in delineating bottom water oxygenation levels. Cutting-edge microstratigraphic and hierarchical sampling coupled with geochemical analyses delineated a spatial distribution for Upper Pennsylvanian black shales in their study.

Geochemical relationships among thinly laminated Carboniferous black shales in the Midcontinent, North America, have been studied in exhaustive detail over the past several decades. Runnels et al. (1953), Vine and Tourtelot (1969, 1970), Coveney (1979, 2000), Cubitt (1979), Heckel (1979), Coveney et al. (1987), Hatch and Leventhal (1992), Schultz and Coveney (1992) and Hoffman et al. (1998) have all significantly contributed to the understanding and classification of these units. These researchers and others have proposed various models in the interpretation of metals siting, diagenetic occurrences, depositional setting, bottom water anoxia interpretations, and variability of redox potential. Zangerl and Richardson (1963) and Heckel (1977) have provided useful perspectives on the depositional settings of

these enigmatic units. Zangerl and Richardson were the first to report metal enrichment values in Pennsylvanian black shales in Indiana with Mo in excess of 1000 ppm.

A widely cited paper by Heckel (1977) invoked a relatively deep, offshore marine setting (maximum transgression) for Midcontinent Pennsylvanian black shales justified by his sea level curve. Coveney and Glascock (1989) inferred a role for basinal brines in the origins of metals in these same units. Coveney et al. (1991) followed this supposition with the hypothesis that other black shale "types" exist and were stratigraphically unique in their position over coal beds, implying shallow water, and nearshore deposition. Schultz and Coveney (1992) further demonstrated the characterization of black shale "types" based on geochemical parameters, including the application of DOP. Hoffman et al. (1998), used microstratigraphic relations and statistical methodologies to conclude that paleoecological indicators of DOA do not point to uniform anoxia, but show a slow anoxia grading into a dysaerobic sequence during the late Missourian (when the Muncie Creek Shale was deposited). More recent work by Schieber (2001) has shown that similar black shale deposits elsewhere also show the importance of pyrite enrichment, and indicate the presence of reducing and often anoxic conditions. Further, Schieber (2001) points out that intermittent organic reworking elucidates the high DOP values. It follows that even during ostensibly anoxic conditions (as shown by bulk geochemical analyses) the periods of oxygen deprivation were apparently short-lived. Thus, the controversy regarding depositional setting and duration of anoxicity events remains.

Like many of the earlier works, this research focuses on reporting results for various geochemical parameters and characteristics of the black shales, some of which are enriched in metals and rare earth elements (REEs). Micro-interval sampling and interpretation (microstratigraphy) is applied to discern whether punctuated periods of anoxia existed. The application of the research results to other geographic locations lends it usefulness in various geologic settings as these sites undergo more extensive research. Comparisons can then be made between the settings and perhaps the assignment of modern analogues could be accomplished.

1.1. Importance of black shales

Black shales have attracted interest from researchers primarily because of their economic importance in terms of hydrocarbon development potential (i.e., source rocks) as well as metal concentrations (Wignall, 1993). Several black shales stand out as being particularly metalliferous, mostly enriched in U, V, Mo, Pb, Cu, Ni, and Zn (Schultz, 1991). Among these are the Alum Shale of Scandinavia, New Albany Shale of the eastern United States, Mecca Quarry Shale of Indiana and Illinois, United States, and several Chinese Cambrian black shale units (Schultz, 1991), primarily recognized through the research efforts of Coveney (2000). Many workers regard the European Permian Kupferschiefer of Poland as the quintessential metalliferous shale. In addition to the importance of metal concentrations, black shales potentially reveal oxygen-deficient events that occurred during the geologic past.

The last two decades, specifically, have brought publications concentrating on understanding the importance of geochemical and paleoecological associations in order to unravel the enigmas of these perplexing units. Yet despite exhaustive research, black shales continue to be the least understood of the sedimentary units. Less than 30 years ago, Cane (1976) noted "...any consideration of the origin and mode of formation of oil shale (i.e., black shale) must be, with little exception, highly speculative". Bralower (1992) was considerably more optimistic in the outlook, boldly stating, "By the 21st century, these fascinating deposits will no longer be one of the major stratigraphic enigmas". A major dilemma in ascertaining the black shale depositional setting is the lack of recent analogues. Piper and Perkins (this issue) cite examples that include the Cariaco Basin, Golfo Dulco, and numerous fjords at high latitudes. The Black Sea and even Baltic regions have also been proposed, but lack the paleostratigraphic and paleogeographic relations of the Pennsylvanian Midcontinent region (Wignall, 1994). Most recent investigations use interdisciplinary studies to examine new areas of research once thought incomprehensible and provide considerable optimism concerning the development of modern analogues.

1.2. Objectives of study

Similar to other investigations of black shales, this study reports geochemical data for separate speciation (C, Fe, and S) as well as for the whole-rock (e.g., by means of XRF). Variations in the depositional character of black shales deposited during the Carboniferous, specifically in North America, have been documented previously, but the acknowledged variations occur predominantly under oxygen-deficient conditions. The focus of this study is three-fold: (1) to geochemically investigate different types of Midcontinent Pennsylvanian black shales; (2) to classify these black shales into distinct groups using elemental fractions such that other blacks shales may be categorized using the same constraints, and (3) to use the geochemically distinct groups of black shales in order to bring to rest the controversy that Midcontinent black shales are exclusively formed in anoxic waters in relatively deep marine settings. It is to this end that an attempt is now made to resolve any question as to whether Midcontinent Upper Pennsylvanian black shales were deposited exclusively in the deep water euxinic settings or whether a variety of geochemical conditions prevailed and the black shales were deposited under both relatively shallow and deep water settings.

2. Review of geochemical methodology used in the study of black shales

This study utilized a variety of geochemical methods including: C/S plots, DOP calculation, S speciation, the interpretation of metal concentrations, and ascertaining the importance of metal proxies.

2.1. C/S plots

Raiswell and Berner (1985, 1986), Leventhal and Taylor (1990) and Raiswell et al. (1988) are just a few of the many workers who have discussed the roles of total organic carbon (TOC)−S−Fe relationships in reconstructing depositional environments. C/S ratios are influenced by sedimentation rate, availability of metabolized organic matter, availability of reactive Fe to fix sulfides into sediments, and the presence or absence of anaerobic conditions above

the sediment−water interface (Dean and Arthur, 1989). Leventhal (1983) has discussed the relationships of C_{org} and S in order to make inferences about depositional environments in terms of the presence of O_2 (normal marine) or H_2S (euxinic) in overlying bottom water. Similarly, Berner (1970), Raiswell and Berner (1985, 1986) and others have discussed these relationships in similar contexts by plotting TOC, pyritic sulfur (S_{py}) and total iron content (Fe_t) or acid-soluble reactive iron (Fe_{HCl}). Normal marine settings are indicated by a positive correlation between TOC and S_{py}, which passes through the origin (Berner, 1984) (Fig. 1). In contrast, euxinic sediments are typified by high S_{py} values and low TOC, so that an intercept on the S axis results (Leventhal, 1983). Occasionally, S versus TOC plots for euxinic sediments indicate flat (zero) slopes (Raiswell and Berner 1985).

C_{org} versus S plots have been used to imply depositional settings of modern and ancient rocks (Leventhal, 1983; Raiswell and Berner, 1985, 1986). Total Fe versus S plots also have been used in much the same manner by Coveney et al. (1987). Unfortunately, these plots (including TOC versus S_{py}) provide little information on reactive Fe availability, a variable that can fluctuate between samples, basins, and source areas.

Differing behavior of TOC versus S_{py} plots is caused chiefly by different factors that affect pyrite formation in normal and marine and euxinic conditions. In normal marine environments, H_2S necessary for the formation of pyrite is produced by bacterial sulfate reduction below the sediment−water interface (Raiswell and Berner, 1985). Additionally, burial of organic matter is important because it is necessary for in situ sulfate reduction and H_2S formation (Berner, 1970). Therefore, for most normal marine sediments possessing adequate detrital Fe (from Fe coatings on grains), the principal factor in limiting pyrite formation is the amount of organic matter buried (Raiswell and Berner, 1985). Thus, pyrite forms diagenetically resulting in a good correlation between pyrite content and organic matter.

Euxinic sediments possess H_2S above the sediment−water interface as well as within the sediment so that pyrite can form prior to burial (syngenetically) in the water column and at the sediment water interface itself (Raiswell and Berner, 1985). Consequently, as a
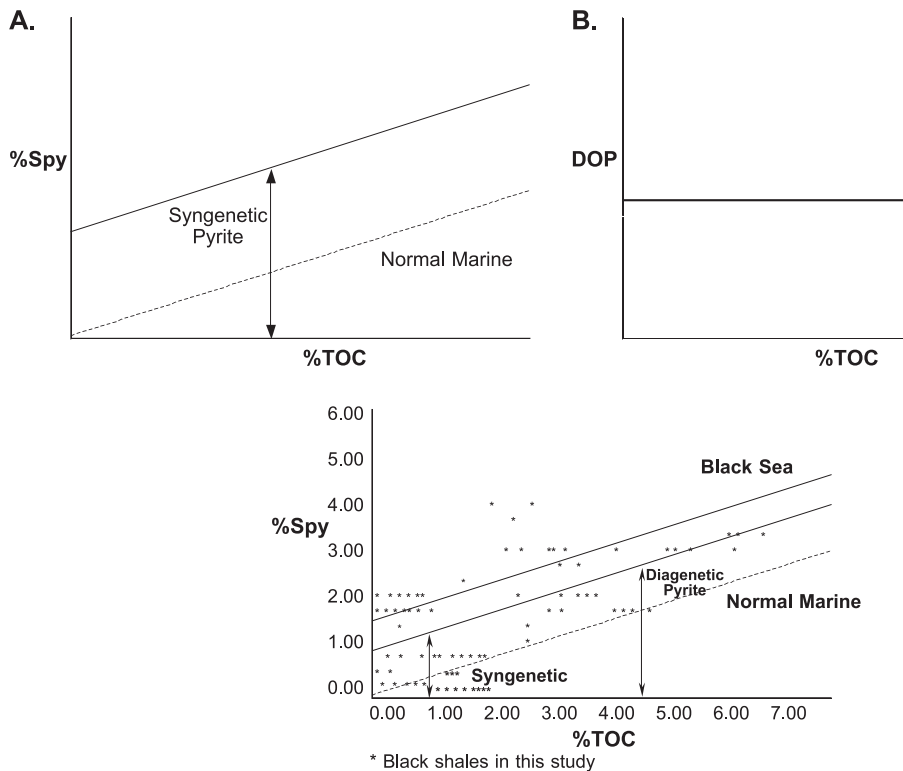
Fig. 1. Plot of percent total organic carbon (TOC) versus percent of pyritic sulfur (Spy) of selected black shales in this study. The Black Sea and "normal" marine regressions are included for reference. (A) represents an idealized plot resulting from the formation of iron-limited syngenetic pyrite while (B) represents an idealized plot of a uniform DOP with increasing TOC. This did not match samples from this study, which showed an increase in DOP with increasing TOC concentrations (adapted from Raiswell and Berner, 1985).

result of the presence of H_2S, C_{org} is not required at the site of pyrite formation. This leads to a situation in which high S_{py} can coexist with low C_{org} content. Thus, the limiting factor in pyrite formation in euxinic sediments is not the C_{org} content (as in normal marine settings), but the quantity of detrital reactive Fe present (Leventhal, 1983; Berner, 1982). Consequently, S is normally better correlated with Fe than with TOC in euxinic sediments.

Unfortunately, a complication results in euxinic sediments when additional diagenetic pyrite is formed. The diagenetic pyrite is C-limited as opposed to the syngenetic pyrite, which is Fe-limited. A TOC versus S plot here results in a situation similar to that of normal marine settings (positive slope), but with a positive intercept on the S axis (Leventhal, 1983; Fig. 1).

In this study, C and S elemental concentrations were measured from the 2.5-cm samples, producing total C and total S values in weight percent using a Perkin-Elmer Carbon Analyzer at the University of Cincinnati. Each sample interval was also pressed into a pellet and analyzed for whole-rock elemental concentrations using a wavelength-dispersive Rigaku XRF spectrometer at the University of Cincinnati. The US Geological Survey geochemical standard SDO-1 (Ohio Devonian Shale) was used as a reference standard in both total C and C_{org} measurements.

2.2. Degree of pyritization (DOP)

In order to adequately discern the influence of Fe availability, reactive Fe contents must be determined, leading to DOP values. DOP is defined as a paleoenvironmental indicator of bottom water oxygenation conditions (Raiswell et al., 1988). It must

be noted that the calculation of DOP was only possible after accurate assessment of total S, TOC, and S_{py} contents. The series of calculations are as follows:

Percentage of organic sulfur ($\%S_{org}$) = 0.20 × percentage of TOC content

Inorganic sulfur (S_{inorg}) = percentage of total sulfur ($\%S_{tot}$) – percentage of organic sulfur ($\%S_{org}$) content

Pyritic iron (Fe_{py}) = S_{py} concentration × (55.85/64.12)

DOP = pyritic iron Fe_{py}/(Fe_{py} + acid-soluble iron (Fe_{HCl}))

where: S_{org} content/percentage of TOC = 0.20 (from Bein et al., 1990).

DOP has the advantage of removing the effects of total Fe on S_{py} concentration (Raiswell and Berner, 1985). The use of the parameter eliminates the effects of total Fe from sediment to sediment and places the emphasis on the reactivity of Fe and H_2S production. Consequently, if DOP values are relatively high, the H_2S concentrations are high and Fe mineral reactivity is greater. In essence, this means a longer duration that H_2S remains in contact with the Fe minerals (Raiswell and Berner, 1985).

DOP can also be related to the redox state of the overlying seawater and microenvironments in the top few centimeters of the sediment (Raiswell and Berner, 1985, 1986). Various terminologies can be applied to the oxygenation levels within environments. Aerobic, oxic, or normal marine (well-oxygenated) water columns generally produce DOP values less than 0.45. Dysaerobic or dysoxic (low O_2 present, but no H_2S) water columns provide intermediate DOP values from 0.46 to 0.75. Bituminous, inhospitable conditions, anaerobic, or euxinic have been applied to water columns containing no O_2, but contain H_2S, with DOP values greater than 0.75. Anoxic is reserved for conditions that are O_2-deficient, but lack sulfidic processes as are present in the euxinic scenario. These boundaries in the bottom water have been applied according to the work of Raiswell et al. (1988).

Essentially, the importance of DOP is in its usefulness in the study of euxinic (and near-euxinic) sediments. In the euxinic scenario, C/S plots yield a positive slope with a positive intercept on the S axis. The non-zero intercept contrasts with the normal marine scenario. Percentage of Corg present plotted versus DOP yields a positive slope in the euxinic situation (as a result of pyrite forming syngenetically as well as diagenetically) compared with a flat (zero) slope on the TOC versus DOP in the normal marine situation. Thus, the two scenarios are separated easily only if DOP as well as C/S ratios are used, but are difficult to separate using C/S plots alone (Raiswell and Berner, 1985; Schultz and Coveney, 1992). However, Lyons et al. (2002) cautions that C/S ratios are vulnerable to weathering during sea level lowstands and thus careful interpretation must be used in conjunction with DOP determinations.

Colorimetric techniques were used for the calculation of DOP in this study. The methodology used in this study is identical to that of Schultz and Coveney (1992) and similar to the method described by Leventhal and Taylor (1990).

2.3. Sulfur speciation

S is present as a ubiquitous component of both modern and ancient marine sediments. Specific S components within these settings differ, but S is usually present as pyrite, acid-volatile sulfides, elemental S, sulfates, S_{org}, or a combination of these (Canfield et al., 1986). S content and composition of black shales can thus be related to the type of diagenetic environment in which the various S compounds were deposited (Goldhaber and Kaplan, 1974). Consequently, it is crucial to accurately quantify S speciation in Midcontinent Pennsylvanian black shales to aid in the determination of diagenetic processes and decipher if indeed, euxinicity was a mainstay of Pennsylvanian seas or if anoxic conditions were punctuated by periods of more oxygen-rich episodes.

The methodology of S speciation in this study used a Cr reduction technique described by Canfield et al. (1986), and modified by Okita (1987), Liu (1988), and described by Schultz and Coveney (1992). It should be noted that this technique represents the most efficient and reproducible method to obtain inorganic sulfide-S data. As a result of the high contents of pyrite in the Pennsylvanian black shales of this study, it was necessary to modify

procedures of Canfield et al. (1986). Modifications in this study center on the use of Zn shot as compared with Canfield et al. (1986), Okita (1987) and Liu (1988) who all used Zn powder, which tended to flocculate, making transfers of $CrCl_3$ solution difficult. Additionally, a further modification used a stopcock technique for introducing the reagents opposed to the syringe methods of other workers.

2.4. Metal concentrations

Instrumental neutron activation analysis (INAA) was used to determine the quantities of trace metals and REEs in the black shale samples, as performed by XRAL Laboratories in Ann Arbor, Michigan. Detection limits and errors are reported in Schultz and Coveney (1992). One difficulty encountered in the comparison of the REE data is the "odd–even effect", in which even numbered lanthanides are more abundant than those with odd-numbered atomic numbers. The abundance pattern selected for normalization of the samples was the North American Shale Composite (NASC) and Post-Archaean Average Shale (PAAS) methods. These patterns are generally taken to represent the upper continental crust after exposure to weathering and erosion (most similar to the Pennsylvanian black shales in this study). The preference for the use of PAAS over NASC (composite) is based on the potential for inclusion of aberrant material in composite samples. Schultz and Coveney (1992) discuss the REE relationship in detail, thus the discussion of REEs in not presented here.

2.5. Geochemical proxies

A geochemical proxy is most accurately defined as some concentration, ratio, or comparison of concentrations that may be used to indicate a particular chemical condition or that a certain process has occurred (Ripley, personal communication). Important proxies in this study included the correlation of C with S and Fe, V and Ni associations, and a summation of metals (including Cr, Mo, V, Ni, and Zn). Various proxies besides these have been used (Hoffman et al., 1998; Lyons et al., 2002), but the aforementioned proxies provided the strongest relationships and were deemed most revealing to this study.

3. Sample methods and statistical techniques

3.1. Sampling scheme

Black shale samples utilized in this study were collected from both outcrop and core samples. Outcrop samples of the Heebner- and Shanghai-type black shales (Schultz, 1990) were collected from various exposures in Missouri, Nebraska, and Kansas. A total of 175 outcrop and core samples from 37 locations were used in the study (Fig. 2).

The sampling scheme for outcrop samples consisted of tracing individual units along strike in eastern Kansas, southeastern Nebraska, and west-central Missouri. Middle Pennsylvanian black shales were collected in several locations in west-central Indiana near the type sections, as described by Zangerl and Richardson (1963) in the vicinity of Mecca, Indiana. Samples collected are representative of fresh surfaces, nearest the water table (if evident) where repeated wetting and drying is at a minimum. Extreme caution was taken during the collection process to sample the least weathered samples available. Channel samples (microstratigraphic sampling) were collected in several locations to fully characterize the vertical succession of the units.

3.2. Sample preparation

Within the black shale study units, outcrop samples were collected at intervals of 2.5 cm for detailed geochemical analysis throughout the entire thickness of the black shale members. Likewise, each core interval was divided into 2.5 cm intervals and sampled. Each interval was split in half lengthwise such that one portion was powdered and used for geochemical analyses and the other portion was used for observation of sedimentological features, paleontological interpretation, and general lithologic fabric. Based on the limited quantity of the samples, some intervals did not contain enough material for exhaustive geochemical analysis, therefore; only essential geochemical testing was accomplished on those sample intervals.

In an effort to minimize oxidation, samples were powdered to -400 μm immediately following sample collection. It was determined by microscopy that
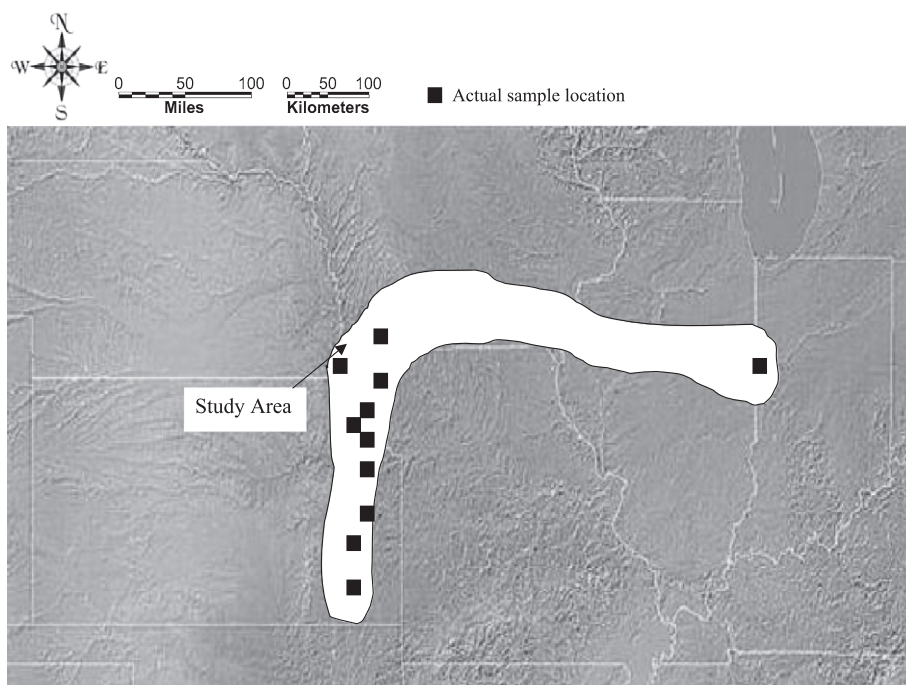
Fig. 2. Sample locations for the study of black shales.

two to three minutes of crushing in a tungsten carbide (WC) mill crusher produced uniform − 400 mesh powders. Observation under a standard petrographic microscope confirmed that grain sizes were consistent among mineral types in the black shale samples. Powder samples were then stored in Nalgene containers for later analyses.

3.3. Statistical techniques

One of the most widely used multivariate procedures in the earth sciences is the discriminant function (Davis, 1986). Discrimination of samples is determined using the linear combination of variables that provides the maximum difference between two or more groups (Davis, 1986), or in this instance black shale "types". In order to determine which characteristics were most useful in separating Midcontinent Pennsylvanian black shale "types", it was necessary to discriminate accurately between black shale geochemical parameters. Data from samples were treated by stepwise discriminant analysis using the Statistical Package for the Social Sciences (SPSS).

Classification is internally based and does not depend on the a priori knowledge of groupings, as does the discriminant function (Davis, 1986). The number of groups in a discriminant function is established prior to the analysis and each sample is treated separately; each sample is provisionally assigned a well-established group (i.e., black shale "type"). In one sense, a discriminant function can be thought of as a way of collapsing a multivariate problem into a univariate problem. If one is able to make a few assumptions about the nature of the data involved in the analysis, a test of separation significance of the groupings may be accomplished. An idea of effectiveness of the variables as discriminators can be gained by computing standardized differences, which can be thought of as a general guide to the discriminating power.

Statistical analyses of geochemical parameters in this study of Midcontinent Pennsylvanian black shales include: multiple discriminant analyses, cluster analysis, and principal components analysis (PCA). The initial step of the multivariate analyses is the formation of a Pearson correlation coefficient matrix be-

tween all geochemical parameters (variables) within groups (black shale "types"). Construction of the correlation coefficient matrices forms a preliminary working model indicating which variables are most statistically significant in the separation of black shale "types".

In this study, the black shale types are well established (Schultz and Coveney, 1992). Variables are represented by various measured geochemical parameters (major oxide percentages, trace element quantities, DOP values, percentage of TOC, Fe ratios, and various other proxies previously determined to provide significance as to depositional or environmental settings). Linear combinations of the elements (canonical discriminant functions or CDFs) are computed and used to maximize the separation between the black shale types. The greater the power of the discriminant functions to separate the black shale "types", the greater the ability to accurately classify unknown samples with a high degree of certainty (DOC). The maximum number of CDFs that can be used is equal to the number of groups, (e.g., three in the instance of black shale "types"), minus one, or the number of discriminating variables, whichever is less. Only the first two functions that account for the greatest variance within the variables need to be used. The customary statistical methodology of multivariate analysis of variance (MANOVA)/Wilks' Lambda method was used to compute this.

Following the stepwise regression to reveal variables most significant to the separation of the black shales, an R-mode cluster analysis of matrices of Pearson correlation coefficients was undertaken. This created groups or clusters in the form of dendrograms, which were then, in turn, compared to a priori black shale groupings or "types" from the discriminant function analysis (DFA). The ultimate objective of this technique was to statistically reveal exactly what quantitative differences exist between black shale groups and decipher underlying proxies and geochemical parameters that were important during (or after) black shale diagenesis.

4. Stratigraphic and paleogeographic setting

The bedrock geology of the North American Midcontinent (including eastern Kansas, southeastern Nebraska, and west-central Missouri) is characterized by laterally persistent Middle and Upper Pennsylvanian carbonates (predominantly limestones) punctuated by marine shale interbeds and thick, silty to sandy shales, with localized channel sandstone development. The Pennsylvanian units strike north–northeast to south–southwest and dip gently westward into the subsurface. Black shale members are distinctive units present in the Midcontinent North American Pennsylvanian strata in the pivotal portion of maximum transgression (Heckel, 1979). Coveney and Glascock (1989) reiterate from Swanson (1960) that up to 40 black shale units occur in the Midwest. Some can even be stratigraphically correlated across the Midcontinent (Wanless and Weller, 1932) and many are considered to be metalliferous by Vine and Tourtelot (1969) on the basis of semi-quantitative spectrographic data.

4.1. Stratigraphic setting

The Pennsylvanian System in eastern Kansas comprises 49 formations that are subdivided into 130 formally named members and aggregated into eight groups and three stages of the Middle and Upper Pennsylvanian (Fig. 3). In this study, units from the DesMoinesian (Middle Pennsylvanian), Missourian (Upper Pennsylvanian), and Virgilian (Upper Pennsylvanian) Stages were examined and are comprised of 10 black shale members from five groups. Most of these units were recognized, defined, and described by R.C. Moore in the late 1930s and 1940s.

At the base of the exposed Pennsylvanian stratigraphic section is the Middle Pennsylvanian (Desmoinesian), which consists primarily of shale, thin coal seams, localized sand channels, and thinly bedded marine limestones. The Missourian Stage (Upper Pennsylvanian) overlies the Desmoinesian (Middle Pennsylvanian) and is characterized by shale, local sands, and thin limestone development. The Virgilian Stage (Upper Pennsylvanian) overlies the Missourian Stage and includes sandy shales and thick limestones with thin marine shale members. The uppermost Pennsylvanian includes an alternation of thicker and more prominent sandy shales, usually with coal and thinner, more compact limestone. The Virgilian Stage is overlain conformably by the Lower
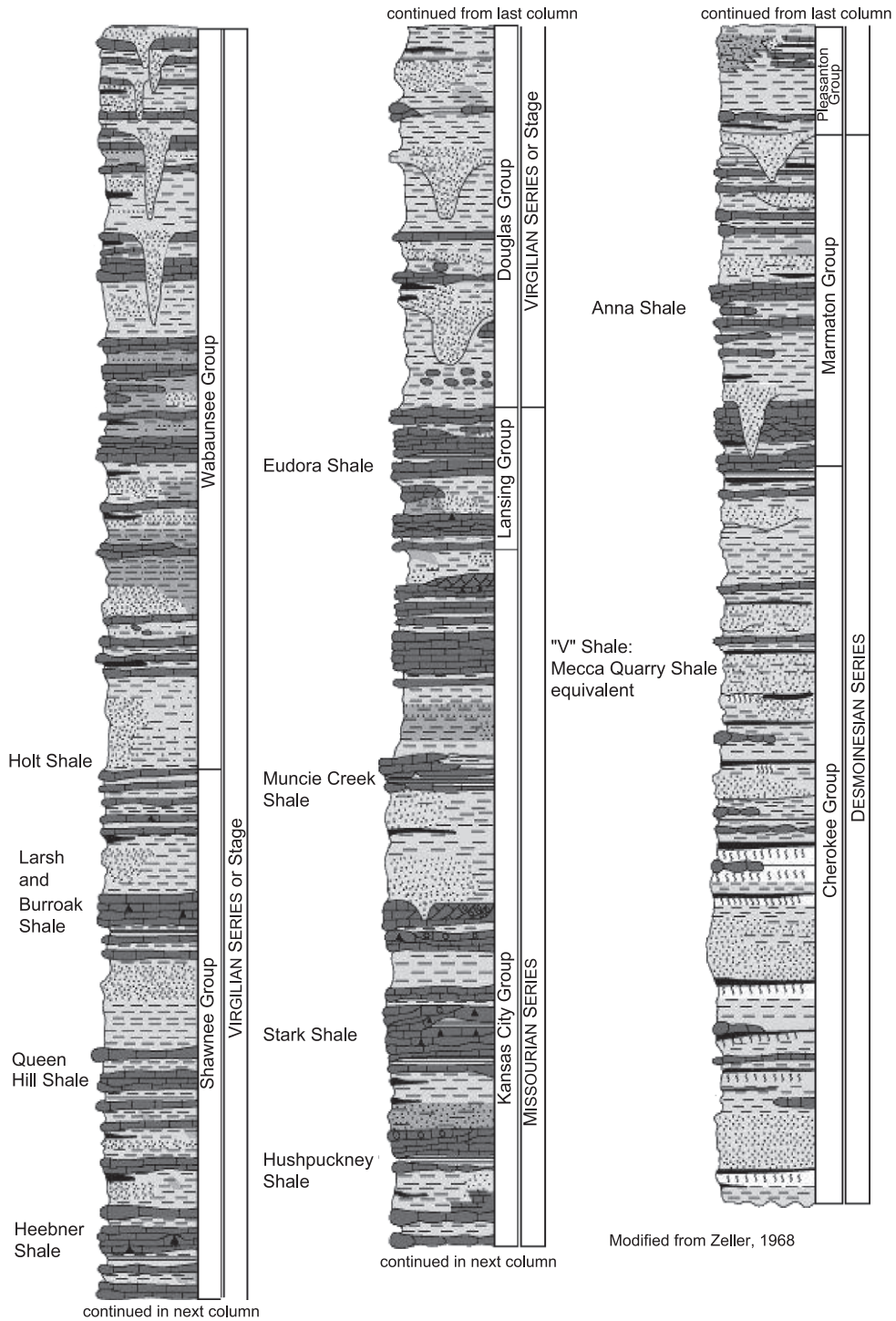
Fig. 3. Generalized stratigraphic column of black shale members in this study (modified from Zeller, 1968).
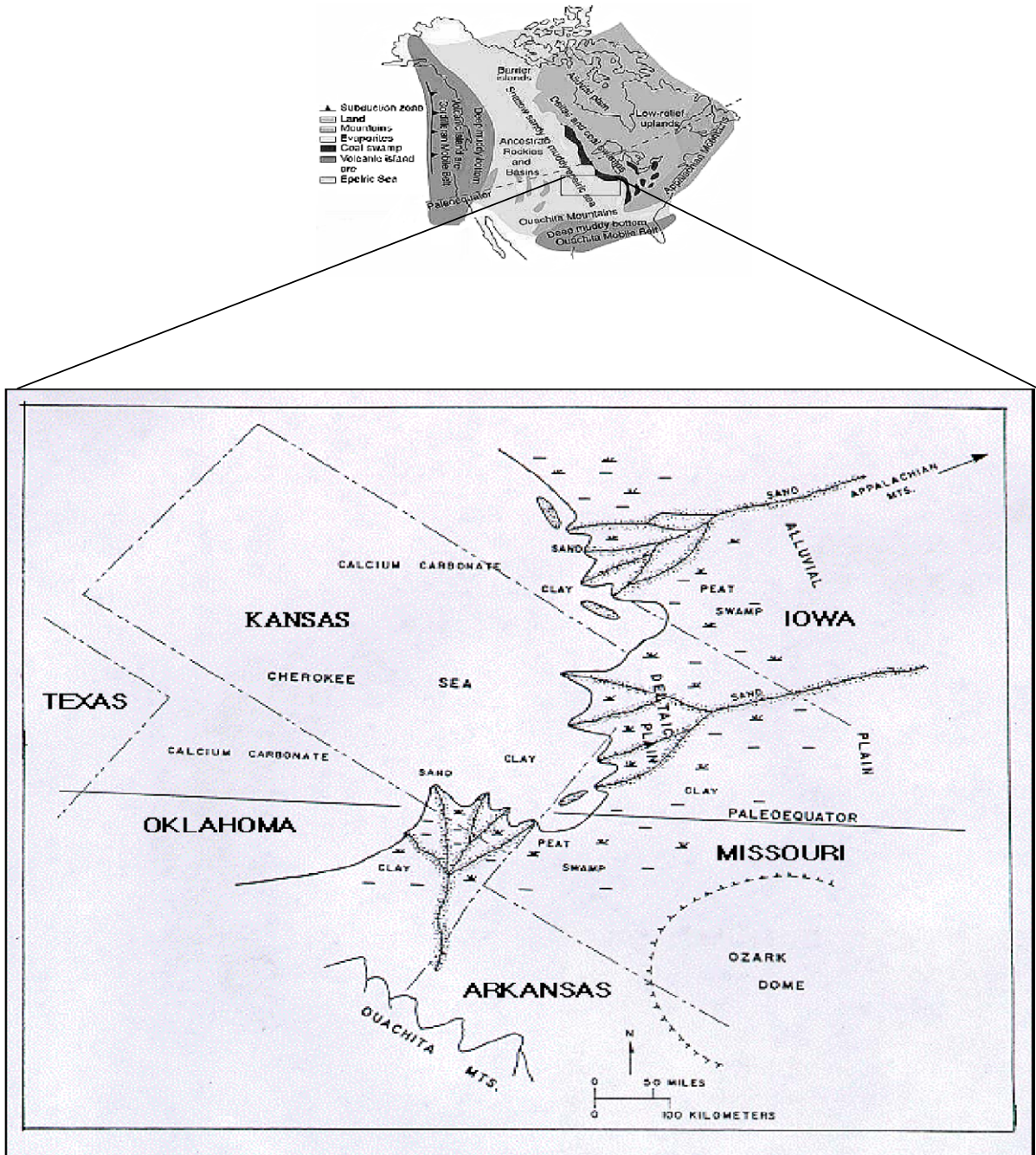
Fig. 4. During times of maximum transgression, the Pennsylvanian seas covered portions of Indiana, Illinois, Iowa, Nebraska, Missouri, and Kansas (adapted from http://www.umkc.edu/sites/env-sci/module8/weblab8.htm).

Permian sequences that continue the general shale-limestone cyclicity.

4.2. Paleogeographic setting

The Pennsylvanian was a time in which epeiric seas inundated the North American craton depositing interbedded limestones and shales in response to static sea level changes (Heckel, 1986; Klein and Willard, 1989) resulting in cyclic sequences. Repeatedly, the seas transgressed and regressed over Midcontinent North America, inundating peat swamps/lagoons, and depositing organic-rich, usually metalliferous black shales (Coveney and Shaffer, 1988). Normal seawater (Holland, 1979) or upwelling bottom waters (Heckel, 1977) may have provided phosphatic material and metals for the Midcontinent Pennsylvanian black shale units, although there may have been other sources. During times of maximum transgression during the Pennsylvanian, west-central Indiana was situated at the eastern margin of an epeiric sea that covered west-central Indiana, central to southern Illinois, southern Iowa, extreme southeastern Nebraska, northern Missouri, and eastern Kansas (Fig. 4). Each cycle contains a black shale member generally interpreted to represent the most transgressive phase of the cycle (Heckel, 1979). In Kansas, where more marine conditions prevailed during this time, Pennsylvanian

strata contain little coal, but more marine sequences exist. Further eastward, shallower conditions prevailed during this time, as evidenced by the type of organic matter present in Indiana as part of the Middle Pennsylvanian Mecca Quarry Shale Member (Coveney et al., 1987; Coveney, 2000).

Both Hallam (1967) and Heckel (1977) have noted that black shales may be deposited in deep- or shallow-water conditions. Heckel (1977), who concentrated on Missourian black shales, reported that the organic-rich deposits were laid down at a slow rate of sedimentation in a relatively deep-water regime. However, Heckel (1977) focused on the westernmost portion of the Pennsylvanian epeiric sea and opposed Zangerl and Richardson (1963) who earlier researched Desmoinesian beds of west-central Indiana and concentrated on the easternmost extent of the Pennsylvanian sea. Zangerl and Richardson (1963) favored extremely rapid deposition in a shallow lagoon-type sequence for the organic-rich deposits in that region.

According to Coveney and Shaffer (1988), from their study of S isotopes in the Pennsylvanian shales of the Midcontinent, conditions were more likely to have been uniform offshore during the Desmoinesian and later in the Missourian Stage when shales were deposited in a slower, relatively deep marine setting. Thus, Upper Pennsylvanian black shales may be differentiated from the Middle Pennsylvanian black

Table 1
Summary of geochemical results for midcontinent Pennsylvanian Black Shales

	Organic data							Inorganic data and metal proxies						
	TOC	S_{py}	Fe_{Py}	S_{org}	S_{tot}	DOP	C/S	V	Ni	Mo	Cr	Zn	V/(V+Ni)	Sum of Cr+Mo+V+Ni+Zn
SDO-1 from Kane et al., 1990	6.90				5.30		1.88	160.00	100.00	134.00	66.00	64.00	0.62	524.00
SDO-1 from this study	10.13	5.26	4.58	0.05	5.31	0.71	1.91	170.00	97.00	160.00	110.00	63.00	0.64	600.00
SDO-1 from Coveney, 2000	<9.95				5.30		1.88	160.00	100.00	134.00	66.00	64.00	0.62	524.00
Avg. Shanghai-type shales (n=20)	2.92	0.56	0.55	0.02	0.65	0.27	15.29	170.00	200.00	5.00	370.00	110.00	0.46	855.00
Avg. Heeber-type samples (n=111)	14.15	1.02	0.96	0.06	1.65	0.40	8.58	742.00	228.00	162.00	647.00	1974.00	0.76	3753.00
Avg. Mecca-type (n=44)	25.15	2.48	2.33	0.18	4.19	0.66	6.00	2121.00	325.00	1874.00	175.00	1310.00	0.87	5805.00
Average of all black shales in this study (n=175)	14.07	1.35	1.28	0.09	2.16	0.44	9.96	1011.00	251.00	680.33	397.33	1131.33	0.70	3471.00

TOC = total organic carbon in weight percent; S_{py} = pyritic sulfur; Fe_{Py} = pyritic iron; S_{org} = organic sulfur in weight percent; S_{tot} = total sulfur in weight percent; DOP = degree of pyritization; C/S = organic carbon/total sulfur in weight percent; V = vanadium in ppm; Ni = nickel in ppm; Mo = molybdenum in ppm; Cr = chromium in ppm; Zn = zinc in ppm; n = number of samples analyzed.
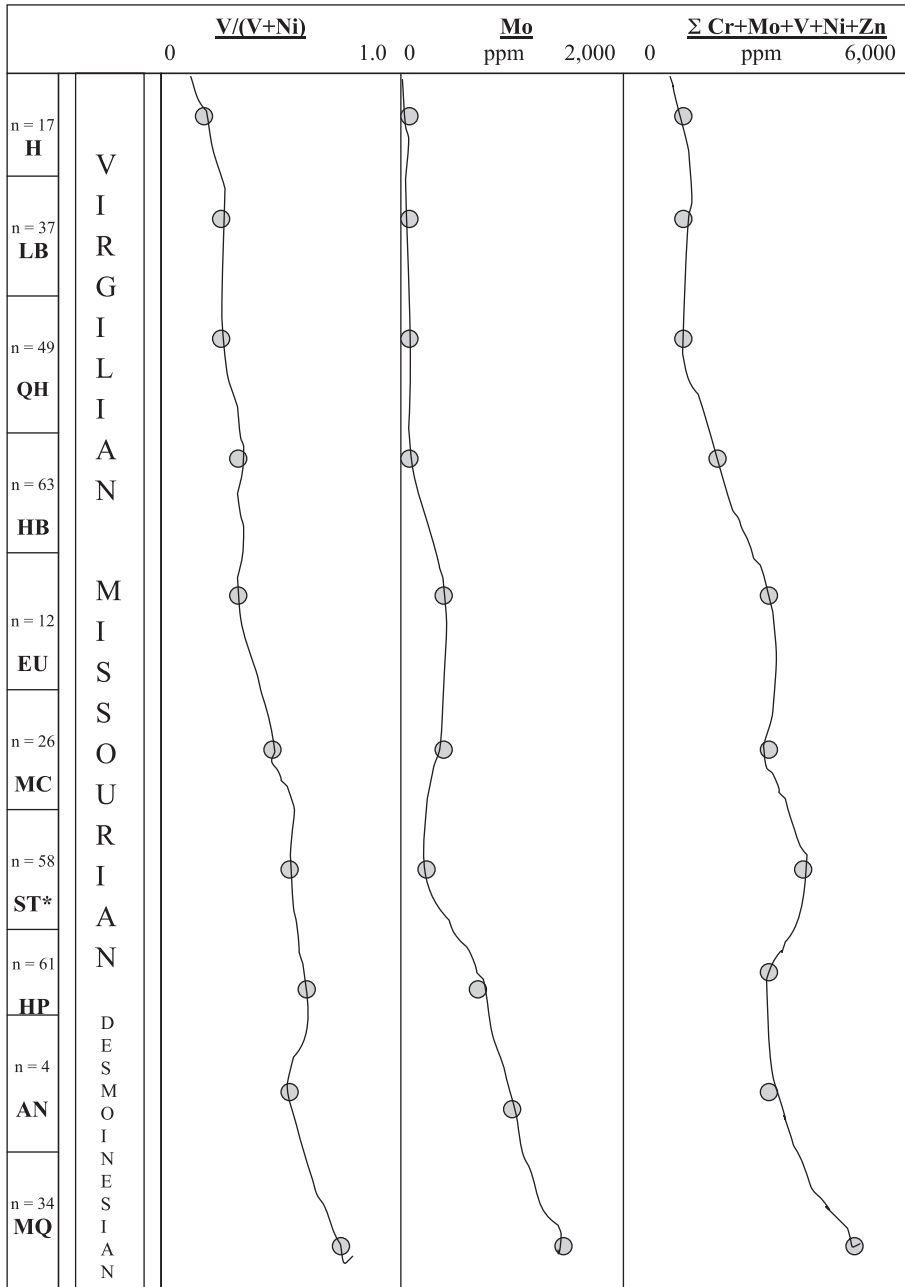
Fig. 5. Mean values for various metal concentrations and proxies in Desmoinesian, Missourian, and Virgilian black shales in this study. Note the relative decrease with time in the concentration of metals. This is an indication, when combined with Fig. 8, that conditions were comparatively less oxygenated and promoted a higher concentration of metal fixation in connection with higher organic matter productivity during the Desmoinesian. This is compared with the relatively low concentration of metals during the Virgilian, which is interpreted to be a time of organic preservation. (n = number of samples). H = Holt Shale; LB = Larsh and Burroak Shale; QH = Queen Hill Shale; HB = Heebner Shale; EU = Eudora Shale; ST = Stark Shale; HP = Hushpuckney Shale; AN = Anna Shale; MQ = Mecca Quarry Shale. *Includes data (four interval samples) from Hatch and Leventhal (1992).
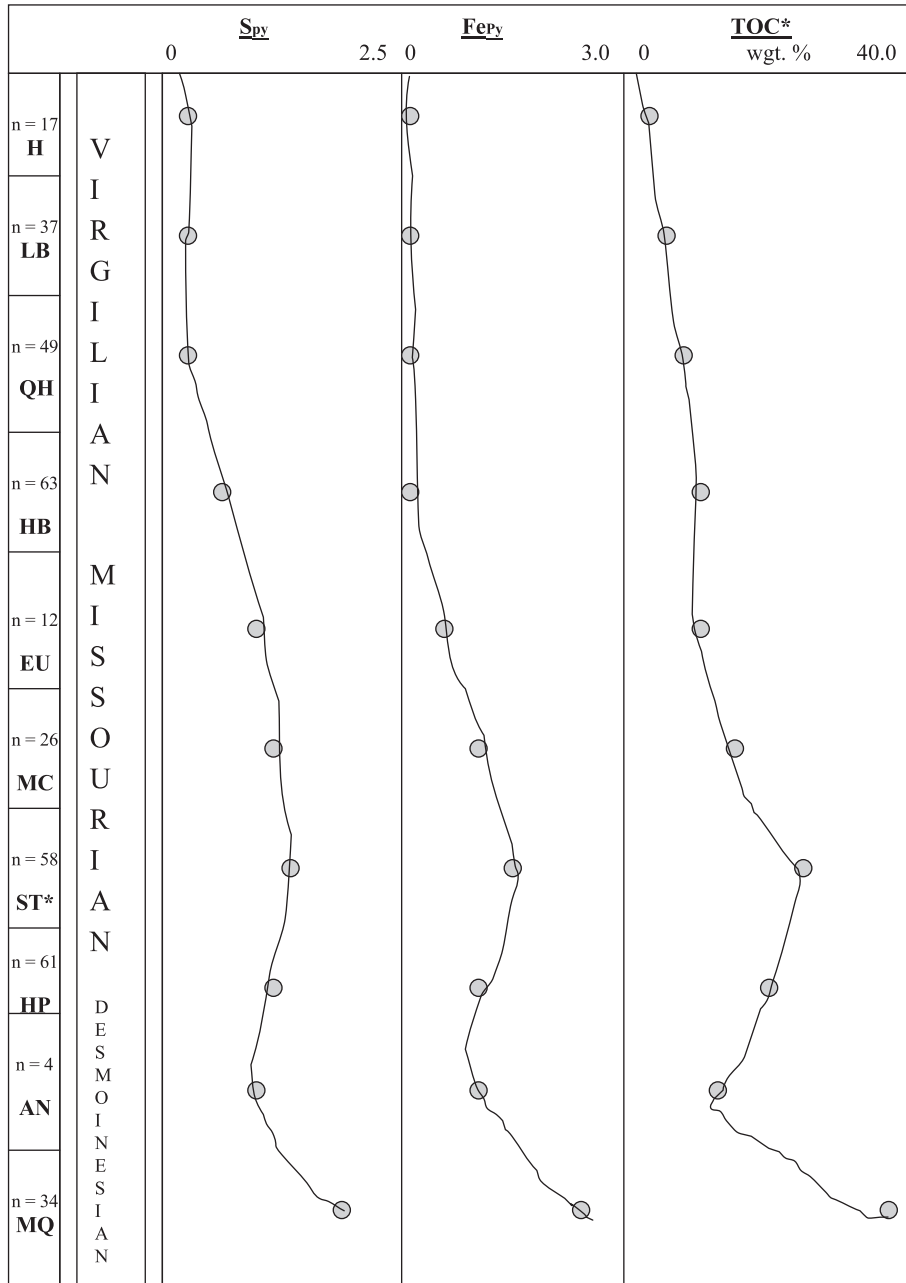
Fig. 6. Mean values for various organic parameters in Desmoinesian, Missourian, and Virgilian black shales in this study. Note the relative decrease with time in the pyritic iron (Fe_{Py}) and pyritic sulfur (S_{py}). This is an indication, when combined with Fig. 7, that conditions were comparatively less oxygenated and promoted a higher affinity for pyrite formation in connection with higher organic matter productivity during the Desmoinesian. This is compared with the relatively low level of pyrite formation during the Virgilian, which is interpreted to be a time of organic preservation and increased oxygenation of bottom waters. (n = number of samples). H = Holt Shale; LB = Larsh and Burroak Shale; QH = Queen Hill Shale; HB = Heebner Shale; EU = Eudora Shale; ST = Stark Shale; HP = Hushpuckney Shale; AN = Anna Shale; MQ = Mecca Quarry Shale. *Includes TOC data (four interval samples) for the Stark Shale from Hatch and Leventhal (1992).

shales based on sedimentation rate and depositional setting. Coveney and Shaffer (1988) also noted the maximum depths of successive epeiric seas may have increased with time so that Missourian seas were relatively deeper as compared with Desmoinesian seas. This fits Wanless and Wright's (1978) suggestion that Desmoinesian black shales were deposited in shallower waters than those of the Upper Pennsylvanian. Schultz (1990) further suggested "progressive ventilation" with time as a mechanism that may have developed in response to a more open system in the Late Pennsylvanian and into the Permian.

All in all, the temporal and spatial paleogeographic setting of the Midcontinent Missourian was one of general desiccation, expressed as longer drying seasons with shorter wet seasons (Shutter and Heckel, 1985). Possible analogues between Missourian paleoclimates and similar transitional climates may include: the deltaic regions of Bangladesh, northern Australia, and regions of northwestern South America. Vegetation patterns include coastal swamps and marshes, forests on floodplains, and savannas in the surrounding areas (Shutter and Heckel, 1985). In a river-borne, clastic-dominated sequence, a chenier plain may form, while away from the clastic influence, carbonate deposition with a range of shallow water depositional sequences would extend offshore adjacent to the shoreline. These types of climatic conditions are also typical of adjacent coastal upwelling areas, as in the northwestern coast of South America (Brongersma-Sanders, 1971).

Although general drying climatic conditions occurred during the Missourian, it should be noted that this did take place suddenly (Shutter and Heckel, 1985). In fact, many of the sedimentological and clay mineralogical features present in the Missourian are present in the Desmoinesian as well. The interpreted wetter conditions during the Virgilian may or may not contradict the prevailing drying pattern. Despite the predominance of coal formation of the Midcontinent and eastern Midcontinent, the Virgilian could represent a relatively wet period reflecting only localized changes as a result of paleotectonic activities. The change in coal character may reflect slower, or a lack of, marine transgressions in the Virgilian, giving rise to coal formation, but not necessarily related to overall climatic conditions during that time period (Shutter and Heckel, 1985).
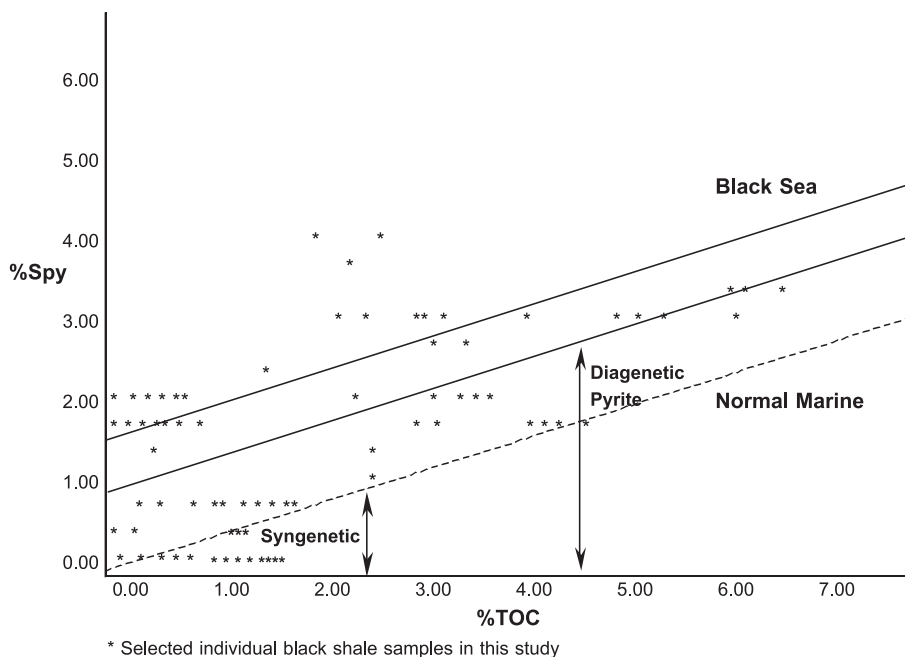

Fig. 7. Scatterplot of weight percent C_{org} versus weight percent S_{py} content. The "normal" marine regression line was constructed using a mean C/S ratio of 2.8 ($\pm$ 0.5%) according to Goldhaber and Kaplan (1974), Berner (1982) and Raiswell and Berner (1986).

5. Results

A summary of geochemical results for the samples is listed in Table 1. The diagrams in Figs. 5 and 6 indicate geochemical variations with depth. Temporal element variability in the black shales samples is significant, both in core and outcrop samples. It is evident, based on the extreme variability of the geochemical nature of black shale units with time, that "punctuated events of anoxia" (or near anoxia) were interrupted by short-lived dysaerobic to oxic events. Schultz (1989) and others have suggested that the variability of redox potential of the depositional environment was an explanation for metal variability; especially in Upper Pennsylvanian black shales. Hatch and Leventhal (1992) tested this hypothesis for Missourian black shales and concluded that the observed variations in element concentrations and ratios indeed showed significant variations in geochemistry of the depositional environment. Thus, they maintained that chemical variability of the depositional environ-

ments might be related to climatic fluctuations and/or minor sea level changes during generally deeper conditions. This statement corroborates the premise that Midcontinent Pennsylvanian black shale units were not under exclusively deep-water conditions as once hypothesized, but experienced various oxidation conditions and water depths during their depositional history.

5.1. Carbon investigation

Results of TOC analyses indicate a clear distinction between black shale "types". Virgilian, Missourian, and Desmoinesian black shales contained TOC values ranging from 0.01% (gray shales) to 43.24% with an average value near 13.00% (Figs. 6 and 7). Most of the C_{tot} present was determined to be TOC. Only one sample in the study (Upper Pennsylvanian) possessed greater than 10% carbonate carbon (C_{carb}). Most of the Late Pennsylvanian black shales contained significantly less TOC than earlier Pennsylvanian black shales. In contrast,

Table 2
A general comparison of various depositional settings of black shales

		Euxinic	Semi-Euxinic	Normal Marine	Freshwater
Example	Modern: Ancient:	Black Sea (modern) Upper Devonian of Appalachians (ancient)	? Midcontinent Pennsylvanian (ancient)	Holocene sediments Normal marine anoxic sediments	Lacustrine environments ?
Geochemical Parameters					
Sulfur isotopes		Light	Intermediate	Intermediate to heavy	Heavy
Carbon/sulfur ratios		Low (1–2)	Low (1–2)	Moderate (near 3)	High (8–10)
DOP values		High (>0.70)	Moderate to low (7.0 to 3.5)	Moderate (6.0 to 3.5)	Low (less than 4.0)
Pyrite Formation (Typical)		Addition of carbon-limited diagenetic pyrite with high reactive iron; Fe-limited	Erratic; fluctuating	Syngenetic pyrite; reactive iron; carbon-limited	Syngenetic pyrite; reactive iron; sulfur-limited
Bottom water oxygenation		H_2S-laden	Erratic; fluctuating	No H_2S; Oxygen prevalent	No H_2S; oxygen not prevalent
Organic carbon control		Preservation	Combination: preservation and production	Mostly production	Production

Note the lack of a modern analogue for semi-euxinix environments, thus pyrite formation and bottom water oxygenation are predominantly unclear. Compiled from various sources and modified from Schultz and Coveney, 1992.

Middle Pennsylvanian black shales possessed higher TOC values, with the predominance of the C_{tot} present as TOC.

5.2. Sulfur speciation

In the current study, it was observed that Heebner-type samples (early Virgilian and late Missourian in age) averaged 0.40% S_{py} content (Fig. 6 and 0.06% S_{org} content. This is contrasted to average values of 2.48% and 0.18%, respectively, for Mecca-type deposits (Middle Pennsylvanian). The higher values can be interpreted as a more euxinic setting for Mecca-type shales, as compared with a semi-euxinic (limited H_2S present in the water column) setting for Heebner-type deposits.

Shanghai-type samples (latest Virgilian) were indicative of even lower values for S_{py} and S_{org}, signifying increasing oxygenation with time and a ''progressive venting'' mechanism invoked by Schultz (1989, 1990) and Schultz and Coveney (1992) to explain the values. A generalized comparison for depositional settings in black shales is presented in Table 2.

5.3. C–S relationships

For this study, the percentage of TOC present plotted versus DOP values yields a pronounced positive slope for the euxinic setting (as a result of syngenetic and diagenetic pyrite formation) compared with a flat (zero) slope on the total percent-
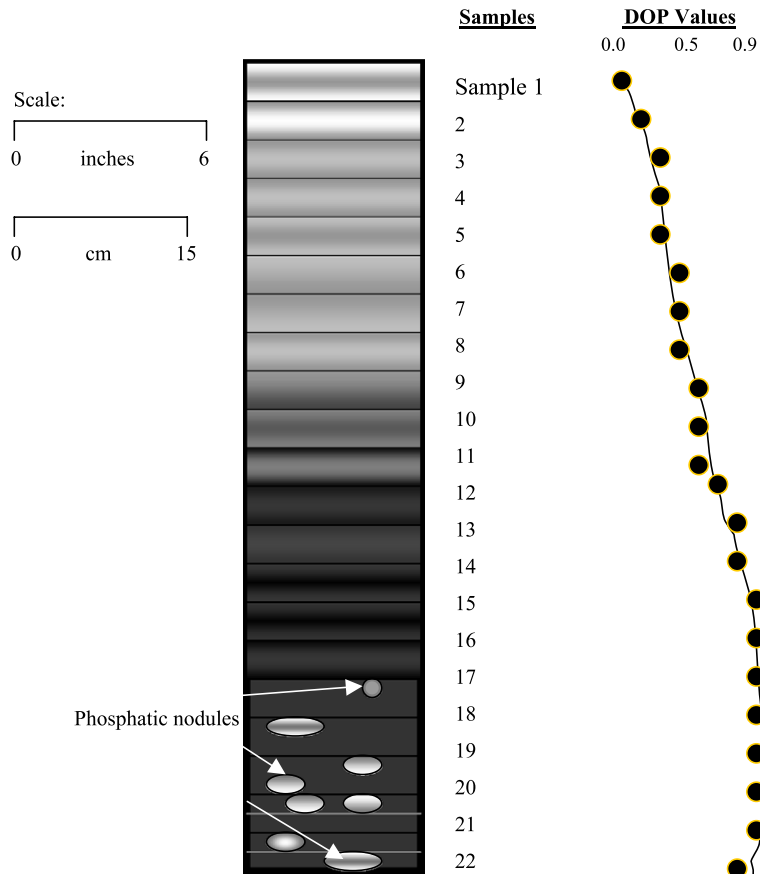

Fig. 8. Example of microstratigraphic DOP determination. Each interval represents 1 in. or 2.5 cm from the base of the black shale to the top of the unit. Both the core sampling scheme and the outcrop sampling scheme were conducted in an identical manner. Typical degree of pyritization (DOP) values are included also. See text for explanation of DOP values.

age of TOC versus DOP in the idealized normal marine scenario (Fig. 1). Thus, the two scenarios were only separated if DOP as well as C/S ratios were used. C/S relationships are summarized in a scatter plot of weight percent C versus weight percent S_{py} in Fig. 7. The ''normal marine regression line'', was constructed using a mean C/S ratio of 2.8 (Goldhaber and Kaplan, 1974; Berner, 1982; Raiswell and Berner, 1986). Heebner-type samples generally plot beneath the normal marine line indicating that the material is not enriched in S_{py} relative to sediments with comparable TOC concentrations that have been deposited under oxygenated bottom water conditions (Fig. 7). DOP shows a pronounced decrease with the passage of time during the Midcontinent Pennsylvanian, interpreted as a decrease in anoxicity with interrupted periods of venting or mixing of O_2 in bottom waters. Fig. 7 graphically depicts this with generally decreasing DOP values with the passage of time.

5.4. XRF: whole rock geochemistry

XRF analyses were undertaken chiefly to accurately assess Fe_{tot} and S_{tot} concentrations preceding colorimetric acid-soluble Fe determination and calculation of DOP (e.g., indications of conditions of bottom water oxygenation). In essence, the XRF results were used to develop a geochemical baseline for the black shale samples. A comparison between XRF measurements at the University of Cincinnati and those conducted at XRAL in Ann Arbor, Michigan revealed consistent analytical precision between geochemical standards (including SDO-1, Ohio Devonian Shale geochemical standard) as well as between Fe_{tot} and S_{tot} samples of this study (Table 1).

Desmoinesian, Missourian, and Virgilian samples indicate a decreasing quantity of S_{tot} with relatively high Fe_{tot} content. Samples closer to the basin center are less enriched in CaO, whereas samples closer to the basin margins are relatively enriched
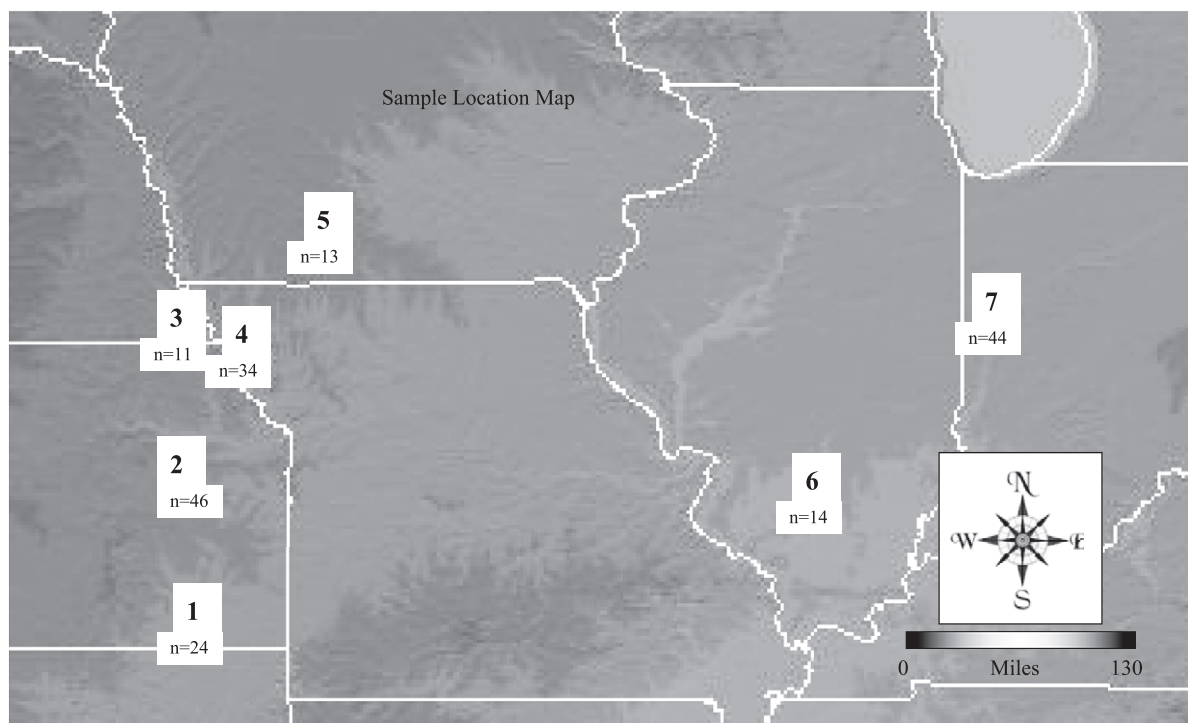

Fig. 9. Spatial depiction of degree of pyritization (DOP), total organic carbon content (TOC), and summation of metals (Co + Mo + V + Ni + Zn) in Midcontinent Pennsylvanian black shales. There is a distinct decrease in time with DOP, TOC concentrations and total metals concentrations from the Desmoinesian through the Virgilian. Desmoinesian samples were not collected from locations 1 through 4. See sample location map for spacing intervals of collected samples (adapted from Schultz and Coveney, 1992).
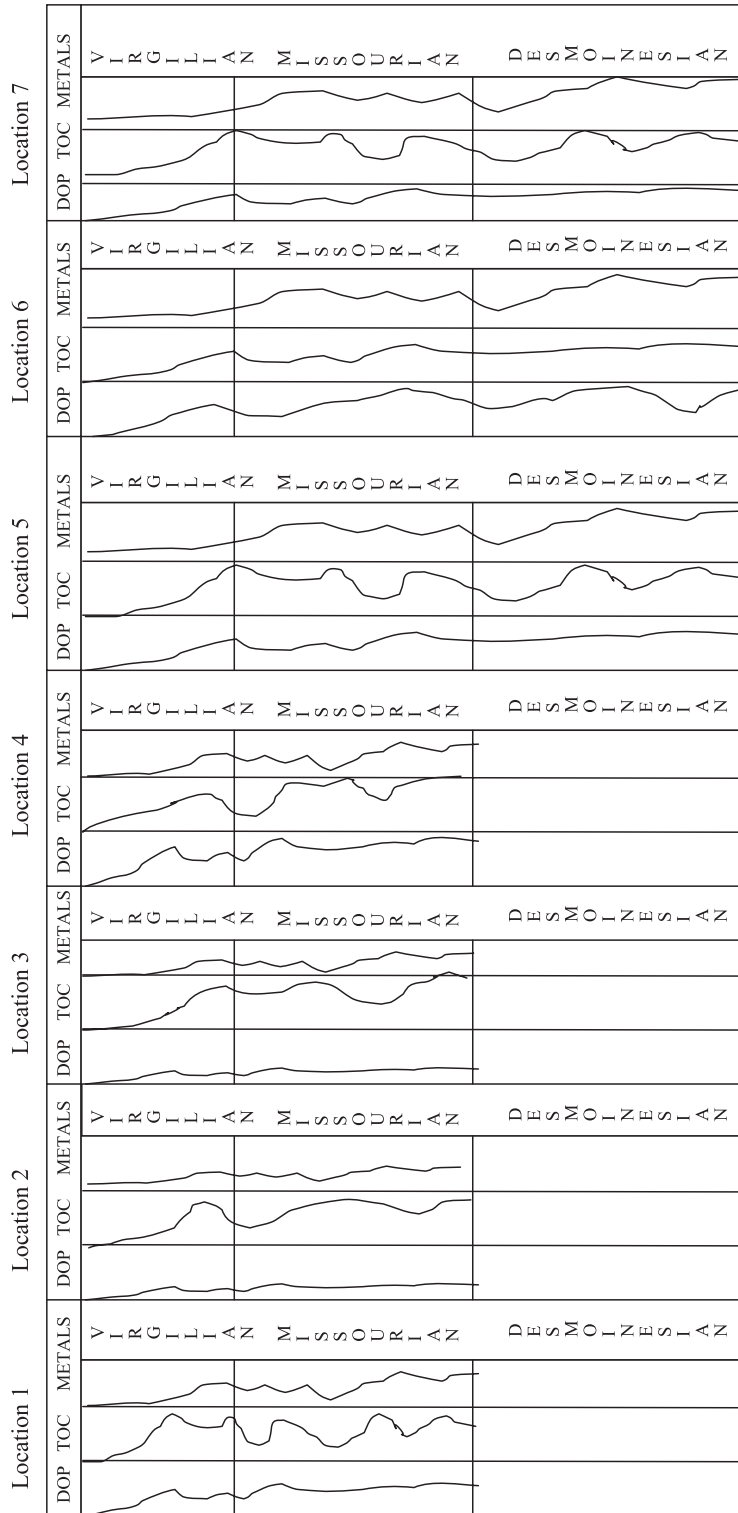
Fig. 9 (*continued*).

in CaO. PO_4 differs in relation to vertical (e.g., stratigraphic) position within individual units. Samples with phosphatic nodules present near the top of the unit indicate elevated P_2O_5 concentrations. This is consistent with observations by Kidder (1985) who notes phosphatic nodules (in Middle and Upper Pennsylvanian black shales) are most pronounced at the top (occasionally at the base as shown in Fig. 8) of black shale units, indicative of the presence of "boundary conditions" between interpreted anoxic and dysoxic conditions (Hatch and Leventhal, 1992).

5.5. Acid-soluble iron and DOP calculation

Analysis of the DOP values for the black shales samples indicates a regional geographic distribution with a greater average DOP value for samples nearer Kansas City, Missouri, a region where samples reflect a closer proximity to the interpreted basin center (Fig. 9). Later Virgilian black shales are indicative of an enhanced oxygenation setting with decreasing DOP values with time. Several samples from southeastern Kansas, interpreted to be a shelf-like setting (Heckel, 1977) reflect an isolated, or even modified lagoonal setting, illustrated by lower DOP values.

Middle Pennsylvanian units (especially in Indiana) are indicative of euxinic settings (high DOP values as defined by Raiswell et al., 1988). Additionally, a positive statistical correlation exists between S_{py} and TOC, S_{py} and DOP, and TOC and DOP (Table 3).

5.6. Metal proxies of relative redox potential

In addition to the determination of DOP, the second measure of relative redox potential for depositional environments is $V/(V + Ni)$, based on research by Lewan and Maynard (1982) and Lewan (1984). An application of their concepts to the whole rock in Midcontinent Pennsylvanian black shales was accomplished by Hatch and Leventhal (1992) and indicated a positive correlation between DOP and $V/(V + Ni)$. This study corroborates their work and includes higher DOP versus $V/(V + Ni)$ values in Missourian and Desmoinesian units (Mecca-type black shales) as compared with Heebner-type units (Virgilian sequences) (Fig. 10).

Table 3
Fractions of black shale types based on correlation coefficients (>0.65)

Elements:	Inferred Fraction	Mean Correlation Between Elements
Shanghai-Type Black Shales		
K, Si, Al, Ti, Fe, Ba, Rb, Na, Th	Detrital	0.91
Mn, Mg, Ca, Sr	Carbonate	0.87
S, DOP, TOC, S_{org}	Sulfidic (weak)	0.66
P, Mo, Se, U, V, Ni, Zn, Cd, Br	REE/P (weak)	0.67
Heebner-Type Shales		
K, Si, B, Al, Ti, Be, Sc, Fe, Ba, Rb, Na, Th	Detrital	0.89
Mn, Mg, Ca, Sr	Carbonate	0.79
S, DOP, TOC, S_{org}, Fe_{Py}, S_{py}	Sulfidic	0.87
P, Mo, Se, U, V, Ni, Zn, Cd, Br	REE/P	0.76
Mecca-Type Shales		
K, Si, Al, Ti, Hf, Sc, Fe, Ba, Rb, Na, Th	Detrital	0.69
Mn, Mg, Ca, Sn	Carbonate	0.71
S, DOP, TOC, S_{org}, Fe_{Py}, S_{py}	Sulfidic	0.91
P, Mo, Co, U, V, Ni, Zn, Cd, As	REE/P	0.88

5.7. Statistical results

Cluster analysis dendrograms (Fig. 11) using the centroid method for black shale groups showed a distinct separation between Mecca-type, Shanghai-type, and Heebner-type black shales. One sample of the Holland Shale was concluded to be an outlier and did not statistically cluster into the black shale "types" (Fig. 11). However, this was only one sample, which reflected an inordinate amount of organic matter (nearly 47% TOC), thus it did lie statistically outside any black shale cluster. These results correlate well with the Schultz and Coveney (1992) study in which black shale "types" were qualitatively assessed, but not statistically analyzed.

Hoffman et al. (1998) recognized fractional associations within the Missourian black shales of the Midcontinent, which included: phosphatic, organic, detrital, and sulfidic fractions. In the current study, the detrital fraction includes major oxides such as
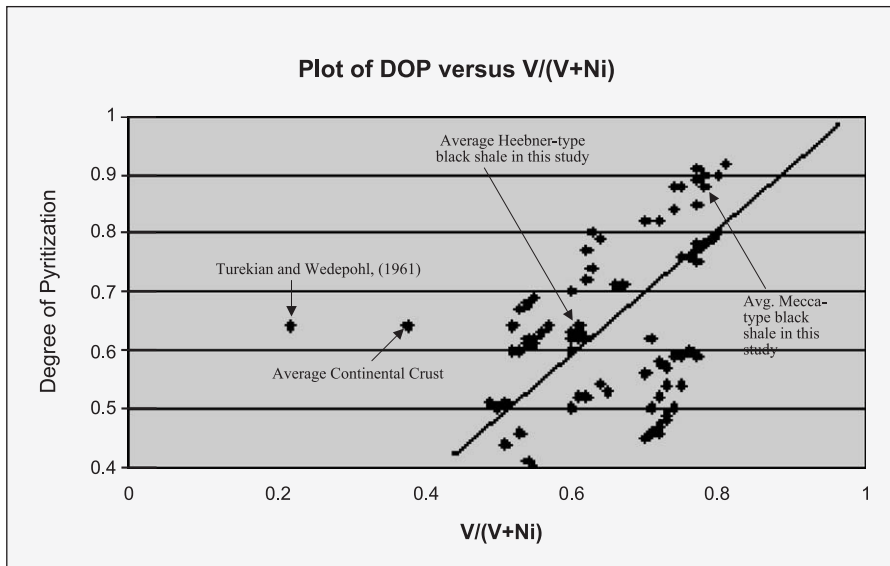
Fig. 10. Scatterplot of V/(V + Ni) versus degree of pyritization (DOP) in samples from this study. Note the positive relationship where a DOP of approximately 0.5 through 0.7 (semi-euxinic) is numerically correlated with V/(V + Ni) values of 0.5 to 0.7. Hatch and Leventhal (1992) noted a similar relationship in Missourian black shale samples from Kansas in which a DOP of 0.70 correlated with V/(V + Ni) values of between 0.70 and 0.80.
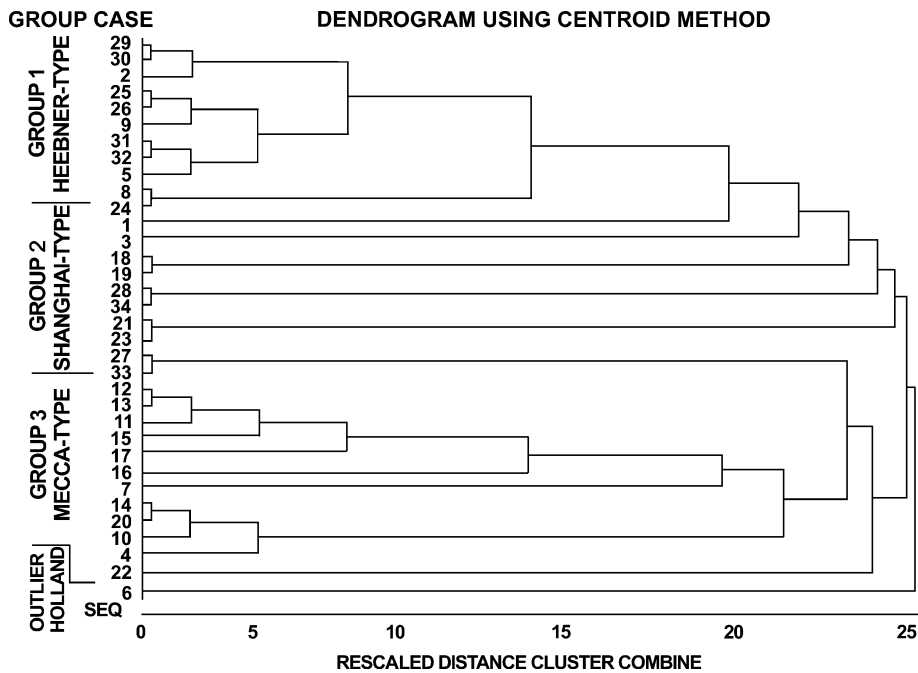

Fig. 11. Dendrogram of samples based on centroid method of Statistical Package for the Social Sciences (SPSS). The grouping of the samples in the left column is based on the R-mode cluster analysis.

TiO$_2$, MgO, Al$_2$O$_3$, Na$_2$O, K$_2$O, Fe$_{tot}$, BaO, SiO$_2$, and ZrO, as well as a "carbonate" fraction (including MnO, CaO, and SrO) as compared with only a detrital elemental association group of Hoffman et al. (1998). This study indicates similar fractions with correlation coefficients greater than 0.65: detrital, carbonate, sulfide, and REE/P. The study of Hoffman et al. (1998) differed only slightly from this study. The only difference between the two studies is that in their study, organic elemental associations were singled out, whereas the current study did not show a statistically valid differentiation between phosphatic and organic associations (Table 3). The organic fraction in the current study featured relatively high correlations among S, DOP, TOC, S$_{org}$, Ni, Cu, V, Mo, and Zn, whereas Hoffman et al. (1998) delineated a separate fraction for "sulfidics".

6. Discussion

The supposition that Midcontinent Pennsylvanian black shales are exclusively products of anoxic bottom water conditions and the products of upwelling of relatively deep marine waters is challenged. Data to support the contention that black shale development in the Midcontinent Pennsylvanian is more geochemically complex than originally determined is offered in this study. This supports the notion that not only were geochemical conditions interrupted by influxes of dysaerobic to oxic waters, but also the correlation of nearshore metal development with geochemical proxies refutes the long-standing "black shale formation with exclusively anoxic bottom-water" association. While it has been shown that strongly O$_2$-depleted conditions do occasionally prevail during earlier Pennsylvanian time (Missourian) as offered by Hoffman et al. (1998), it is now evident that this was not a consistent setting during all phases of the Late Pennsylvanian.

6.1. Interpretations

The diagnosis of oxygenation water conditions in black shales has been delineated by the use of redox sensitive elements. Numerous workers (Lewan and Maynard, 1982; Hatch and Leventhal, 1992; Schultz, 1989) have used the technique of correlating redox element fluctuations in comparison to changing bottom water oxygenation conditions. As an example, Cr, Mo, V, and Ni have been correlated with O$_2$-poor settings because reduced ion species are readily adsorbed onto organic matter or form insoluble precipitates (Pratt and Davis, 1992; Calvert and Pederson, 1993; Hoffman et al., 1998). This study examines metal assemblages and illustrates specific occurrences when the quantity of metal concentrations decreased and likewise, oxygenation levels increased. Hoffman et al. (1998) point out that redox-sensitive process associated with organic matter cycling and metal assemblages often show significant trends in spatial-temporal issues regarding environmental conditions.

The importance of the determination of C$_{tot}$ and TOC within these samples lies in distinguishing organic material types, thus separating black shale "types" and substantiating the premise that conditions responsible for a diverse geochemical history were evident throughout the Pennsylvanian. Additionally, TOC values aid in the determination of bottom water oxygenation conditions and computation of DOP (Schultz and Coveney, 1992).

In the instance of Midcontinent black shales, it is evident that as TOC content increases and oxygenation supply decreases, more H$_2$S forms and increases in disseminated pyrite occur, resulting in higher DOP values. This is graphically depicted in Figs. 8 and 9 where a pronounced decrease in DOP with time is evident. The distributions of dissolved O$_2$, C, and various nutrients in the ocean were strongly affected by production of biomass in the euphotic zone and by a remineralization of particles during settling processes and after deposition at the ocean floor. These processes generally led to surface water nutrient depletion and to higher nutrient/low O$_2$ values in intermediate, deep, and bottom waters. Differences in the vertical structure of various nutrients (i.e., phosphate and TOC) reveal differences in the penetration depths of organic material. Apparently, the production of C$_{org}$ (i.e., decreased biomass) decreased during the late Virgilian time such that black shales contained less TOC with the passage

of time than earlier Missourian and Desmoinesian black shales.

From a paleogeographic standpoint, it is evident that the quantity of major oxides, especially CaO, differs as a function of position within the basin. This supports Heckel's (1977) supposition that in deeper portions of the basin (i.e., Kansas) where more marine conditions prevailed during the Pennsylvanian especially during the earlier stages, a greater quantity of marine sequences (including euxinic black shales) exist. However, it also supports Zangerl and Richardson's (1963) proposition that a shallower water setting existed for black shales in the easternmost extent of the Pennsylvanian seas. This has been interpreted to be the result of increased TOC production during the Desmoinesian when climatic conditions favored the production of organic debris from peat swamps in a nearshore shallow water setting (Coveney, 2000).

As shown by Coveney et al. (1987), Hatch and Leventhal (1992), Schultz and Coveney (1992) and Hoffman et al. (1998), late Pennsylvanian black shales show an impressive array of geochemical complexity. Beginning even with Desmoinesian (Middle Pennsylvanian) time, Coveney (2000) demonstrated a nearshore, yet exclusively euxinic setting for emplacement of various "roll-front" (i.e., bounded on the concave side by altered, oxidized rock) metals. During later Missourian times, Hatch and Leventhal (1992) interpreted predominantly euxinic conditions, punctuated by progressive dysaerobic conditions with time. Hoffman et al. (1998) went so far as to state "bottom water anoxia was most intense in the Stark Shale, intermediate in the Hushpuckney Shale, and least intense in the Muncie Creek Shale". In the latest Virgilian, Schultz and Coveney (1992) demonstrated a predominantly dysaerobic to oxic setting, when geochemical conditions favored fluctuating bottom water conditions and the necessity for varying diagenetic processes, with black shales almost exclusively devoid of the high metal concentrations that were prominent during earlier Pennsylvanian times. All of these works imply variation, including an overall trend towards an increase in oxygenation with time, in bottom water conditions. This substantiates the premise that deep-water, O_2-deficient black shales are not the solitary black shale type in the Pennsylvanian Midcontinent.

6.2. Statistical treatment

From the correlation coefficient matrices, Middle and Late Pennsylvanian black shales show a positive correlation among DOP, Fe_{py}, and S_{py}. This indicates that pyrite formation plays a key role during black shale diagenesis, although the trend does show a statistical decrease in the correlation of these variables with the passage of time (e.g., Desmoinesian to Virgilian). Thus, pyrite formation apparently became a less important diagenetic activity with time into the later stages of the Pennsylvanian in the Midcontinent.

Based on the correlation coefficient matrices of black shale parameters, it is evident that several fractions of elements and geochemical parameters are present in each black shale "type" (Table 3). The differences in the fractions, or what Hoffman et al. (1998) referred to as "elemental associations", indicate that various sedimentological and geochemical processes occurred during diagenesis. This reflects the overall heterogeneity and different depositional environments of black shale "types". Note that this heterogeneity is reflected both temporally and spatially in the black shale samples of this study (Fig. 8).

An interesting facet of the statistical analyses is that it shows a progressive trend towards increasing oxygenation conditions with time as well as decreased metal concentrations in the black shales with time. This is consistent with Schultz and Coveney's (1992) work in which decreasing values for DOP and TOC with time reflect the likelihood of progressive ventilation or other similar event improving bottom water oxygenation conditions, accompanied by reduced rates of terrestrial organic matter input. This greatly contrasts with Heckel's (1977) supposition that marine black shales are exclusively deposited in relatively deep-water settings. Although Heckel suggested a deep-water origin and a role for upwelling bottom waters in 1977, he also hinted that alternative modes of formation might exist and an examination of organic matter in near-shore shales might be germane. Heckel's (1977) suggestion has been most visionary in that others have clearly demonstrated that attributes

of nearshore black shales do indeed exist (Coveney et al., 1991; Schultz, 1990, 1991) in the Midcontinent Pennsylvanian.

7. Summary

This study set out to: (1) investigate different types of Midcontinent Pennsylvanian black shales from a geochemical perspective and discern geochemical changes in key indicators with time; (2) offer a classification scheme to organize these black shales into distinct groups so that other blacks shales may be categorized using the same constraints, and (3) bring to rest the controversy that black shales in the Midcontinent are exclusively formed in anoxic waters in deep marine settings.

The following conclusions have been reached:

1. Through detailed sampling techniques combined with geochemical analyses and statistical operations, it has been shown that the Midcontinent Pennsylvanian black shales show an impressive array of geochemical complexity. A wide range of major and trace element concentrations, combined with widely variable indicators, indicate the presence of varying geochemical settings and that numerous associated chemical reactions occurred syngenetically. This is significant and contrasts with earlier suppositions that during the Pennsylvanian, the Midcontinent included deposition of anoxic, deep water-based black shales formed exclusively in upwelling bottom waters where syngenetic reactions ceased to develop.

2. A pattern of generalized progressive oxygenation (i.e., "ventilation" as offered in Schultz and Coveney, 1992) prevailed from the Middle to Late Pennsylvanian time in the Midcontinent stratigraphic section. DOP values decrease dramatically from the Desmoinesian units to the Virgilian units and provide for a decrease in anoxic bottom water conditions as epeiric seas developed and began to progressively shallow.

3. There is a statistical correlation among averaged values for various geochemical parameters that may be indicative of progressive ventilation conditions during the Pennsylvanian in Midcontinent North America. Statistically derived frac-

tions of elements and geochemical parameters in this study authenticate earlier work by Hoffman et al. (1998) concerning Missourian units. Additionally, fractions for late Pennsylvanian (Virgilian) time are defined.

4. As noted in Schultz and Coveney (1992), three "types" of Midcontinent Pennsylvanian black shales have been confirmed based on statistical clustering techniques. Lithologic characteristics and geochemical parameters justify the typing.

5. Based on the extreme variability of metal concentrations in the Midcontinent Pennsylvanian black shales, geochemical proxies, and organic characteristics, punctuated events of anoxia (or near-anoxia) must have been interrupted by short-lived dysaerobic to oxic events. The variability of redox potential of the depositional environments explains the variability of metal present (Schultz, 1990; Schultz and Coveney, 1992).

6. In general, geochemical evidence validated by statistical treatment of data, challenges the once held notion that Midcontinent Pennsylvanian black shales were exclusively deposited under anoxic bottom water conditions.

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