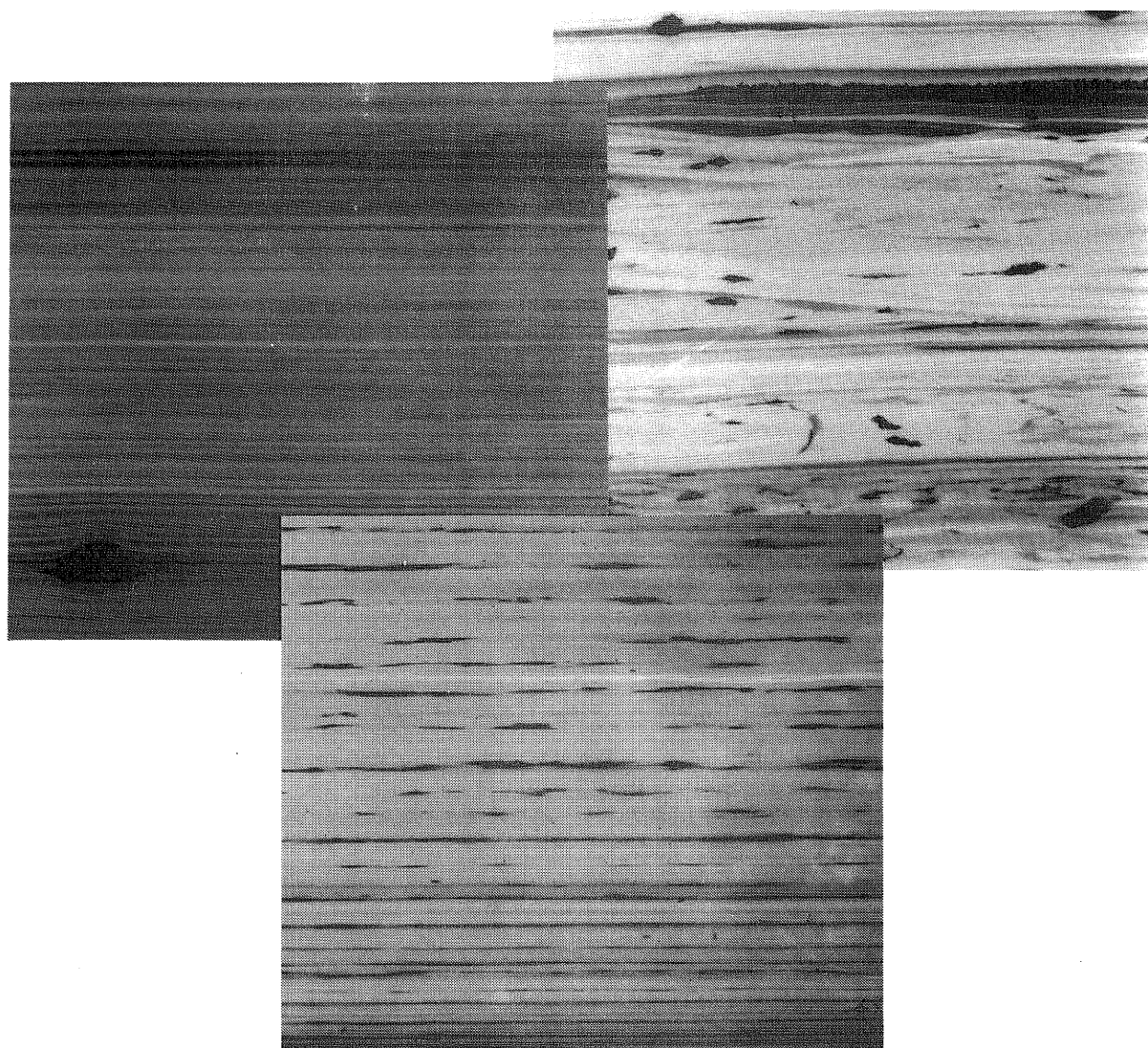# Geochemistry of Black Shales of the New Albany Group (Devonian–Mississippian) in the Illinois Basin: Relationships between Lithofacies and the Carbon, Sulfur, and Iron Contents

Joyce K. Frost

Circular 557 1996

Geochemistry of Black Shales of the New Albany Group (Devonian–Mississippian) in the Illinois Basin: Relationships between Lithofacies and the Carbon, Sulfur, and Iron Contents
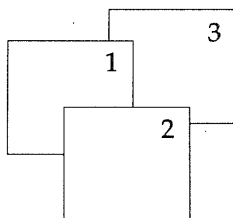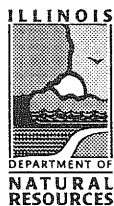
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ACKNOWLEDGMENTS

Cover photos   1 Very finely laminated brownish black Grassy Creek Shale with very fine, even, and closely spaced pyritic laminae. Large black feature at lower left is a pyrite nodule. Sample 01KY01L1, Christian County, Kentucky.   2 Finely laminated Grassy Creek Shale with numerous small pyrite nodules along bedding planes. Sample 02IL05C1, Effingham County, Illinois.   3 Poorly laminated Selmier Shale. Laminae are discontinuous and widely spaced. Several faint silt filled burrows cut across the bedding and truncate laminations. Sample 01KY08C1, Christian County, Kentucky. All photos are at full scale. From Cluff et al. 1981.

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CONTENTS

ABSTRACT

Data used to investigate the geochemistry of depositional environments of shales of the New Albany Group (Devonian–Mississippian) in the Illinois Basin were the organic carbon, sulfur, and iron contents of 216 core samples and 158 well cuttings samples, reactive iron determined on 71 samples, and lithofacies data on the core samples. The positive correlation between total or pyritic sulfur and organic carbon generally found for the 384 samples indicates that the dominant process controlling pyrite formation in these black shales was sulfide production by bacterial reduction of seawater sulfate concomitant with bacterial oxidation of organic matter.

Shale samples with a low organic carbon content (≤2.5%) generally represented dysaerobic or dysaerobic/anaerobic lithofacies types primarily from the shallower western and west-central parts of the Illinois Basin. These samples showed a good correlation between sulfur and organic carbon (ratio of organic carbon to sulfur = 1.4 to 2.2) and between degree of pyritization of reactive iron or total iron and organic carbon. Samples with greater organic carbon content (that is, a more anaerobic lithofacies type) were generally from deeper parts of the Illinois Basin to the east and south and had organic carbon to sulfur ratios averaging about 2.8. Degree of pyritization of reactive iron also increased and total iron content increased slightly as organic carbon content increased. Some samples, mostly from the Grassy Creek Formation, had relatively high organic carbon content, average iron content, and constantly high degree of pyritization of total iron; pyrite formation was probably limited by the amount of reactive iron in these samples.

Sixteen organic carbon-rich samples had unusually high iron and sulfur contents. Although the data suggest pyrite was formed in H_2S-bearing bottom waters in five samples from one core in the deepest part of the Illinois Basin of southeastern Illinois, anomalously high amounts of pyrite probably formed locally during later diagenesis in the other samples.

Samples from the top of the Grassy Creek Shale from the deep part of the Illinois Basin (and one Hannibal Shale sample) had relatively high organic carbon content, a high organic carbon to sulfur ratio averaging 4.8, and high concentrations of vanadium and the chalcophilic elements Zn, Se, Sb, and Ag. The composition of these samples reflects slow deposition in a deepening sea when, at the end of the Devonian or beginning of the Mississippian, the southern part of the Illinois Basin approached sediment-starved conditions.

INTRODUCTION

Investigations of the relationship between organic carbon and pyritic sulfur in marine shales have led to a better understanding of the formation of pyrite in marine sediments and of the depositional and diagenetic histories of many shale formations (Leventhal 1983, Fisher 1986, Leventhal 1987, Donnelly et al. 1988, and Boesen and Postma 1988). Pyrite forms in marine sediments from the reaction of iron (usually from detrital minerals) with sulfide that is formed by bacterial reduction of sulfate from seawater. Anaerobic bacteria use sedimentary organic matter as an energy source and reducing agent. Sulfide is formed only under anoxic conditions. This means that sufficient organic matter must accumulate in the sediment for some of it to remain after all the available oxygen is consumed by aerobic microorganisms, which convert organic matter to carbon dioxide. Part of the remaining organic matter undergoes oxidation, as represented by the simplified reaction

$$2CH_2O + SO_4^= \xrightarrow{\text{bacteria}} H_2S + 2HCO_3^-$$
organic matter
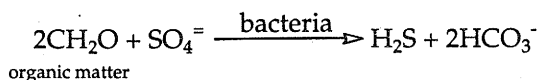
When sulfate reduction in the sediment ceases, remaining organic matter is preserved in this stage of diagenesis. Organic matter may, of course, be decomposed further via fermentation or decarboxylation reactions at greater depth and temperature.

Under normal marine conditions of oxygenated bottom waters, the amount and bacterial metabolizability of organic matter appear to be the most important factors controlling how much pyrite may form (Berner 1984). Sweeney (1972) and Goldhaber and Kaplan (1974, fig. 10) showed, for modern marine sediments, a correlation between organic carbon and pyritic sulfur, with a mean ratio of organic carbon to sulfur (C/S) of 2.8 and an intercept at the origin (fig. 1). The line of correlation passes through the origin because, if no organic matter is preserved, there is no net reduction of sulfate to sulfide and hence no formation of pyrite.

In euxinic marine environments, such as the Black Sea, where bottom waters contain hydrogen sulfide, the metabolic and reduction processes of the bacteria operate on the organic matter and detrital iron suspended in the water column. Iron sulfide forms in the water column or at the water–sediment interface, and an appreciable amount of pyrite is preserved even if little or no organic material reaches the sediment or if the organic matter is largely consumed in the sulfate reduction process within the sediment. Under such conditions, more pyrite is formed per unit of buried carbon (C/S < 2.5), and, as shown in figure 1, a regression line of sulfur on carbon gives a positive intercept on the sulfur axis (Leventhal 1983).

Raiswell and Berner (1985), using data from recent Black Sea sediments and Jurassic shales, demonstrated
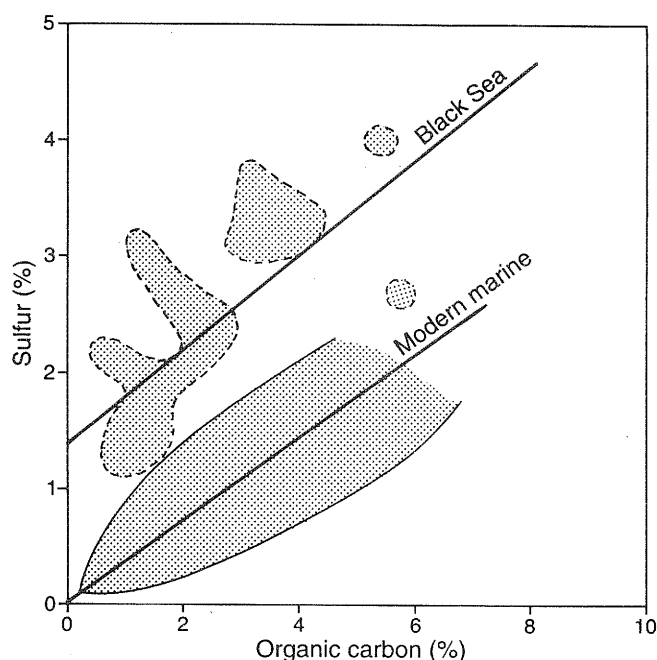
Figure 1 Schematic plot of the carbon and pyritic sulfur relationships in modern marine sediments and in samples from a euxinic environment. The shaded area and regression line for modern marine sediments represent the bulk of the data in figure 10 of Goldhaber and Kaplan (1974). The shaded areas and regression line for Black Sea sediments represent data of Hirst (1974) as interpreted by Leventhal (1983, fig. 1).

that the limiting factor for pyrite formation in euxinic environments is the amount of reactive detrital iron delivered to the sediment. Their conclusion is demonstrated by the lack of a relationship between organic carbon and the iron that exists as pyrite. Degree of pyritization of iron (DOP) may be defined (Berner 1970) as (1) the ratio of pyritic iron to total iron in a sample or (2) the ratio of pyritic iron to the sum of pyritic iron and the nonpyritic iron that is soluble in hot, concentrated hydrochloric acid. The second definition is more precise because nonpyritic iron that is not quickly soluble in hot, concentrated hydrochloric acid is not likely ever to have been available to react with hydrogen sulfide to form pyrite (Berner 1970). All the reactive iron in a euxinic environment is likely to be used in syngenetic formation of iron sulfide in the water column or at the water–sediment interface. Consequently, the degree of iron pyritization does not correlate with organic carbon content in sediments in euxinic environments.

Leventhal (1987) used the relationship between organic carbon and sulfide–sulfur in core samples of Devonian shales from the Appalachian Basin to evaluate the depositional environment of the shales. He concluded that a central area of the Appalachian Basin was euxinic, as implied by the positive intercept on the sulfur axis on the plot of carbon versus sulfur content for cores from that area.

This report investigates the relationships between organic carbon, pyritic sulfur, and the degree of pyritization of iron in shales of the New Albany Group (Middle Devonian–Kinderhookian) in the Illinois Basin. The results, together with lithofacies data, are used to characterize environments of deposition and diagenesis for these shales. This report also examines the relationship between these environments and the unusual increase in concentration of trace metals in the shales at the top of the New Albany Group in the deep part of the Illinois Basin in Illinois. Chemical and lithofacies data are taken from the extensive chemical and geologic studies made of the New Albany Group in Illinois for the U.S. Department of Energy Eastern Gas Shales Project (Bergstrom et al. 1980). In addition, reactive acid-soluble iron was determined in 71 New Albany shale samples.

GEOLOGIC SETTING AND STRATIGRAPHY

The Illinois Basin is shown in figure 2, and the formations of the New Albany Group in Illinois are illustrated in cross section in figure 3. In Indiana and Kentucky, and recently in southern Illinois in the area of the Paducah 1° x 2° Quadrangle (Nelson 1995), the New Albany is classified as a formation. In the remainder of Illinois, it is classified as a group. The group-level classification is retained for this report because most of the data are from the parts of the Illinois Basin outside the Paducah Quadrangle in Illinois.

As described in Cluff et al. (1981), the basal Blocher Shale in southeastern Illinois consists of brownish black to grayish black, finely laminated, dolomitic and calcareous shales. From the unit's generally high organic carbon content and the finely laminated sediments with rare burrows and an absence of megafossils, Cluff (1980) concluded that the Blocher Shale was deposited in a predominantly anoxic deep-water environment.

Overlying the Blocher is the Selmier Shale, which consists of alternating beds of thickly or poorly laminated brownish black, grayish black, and olive gray to olive black shales. At some locations, the Selmier comprises indistinctly bedded, dark greenish gray to olive gray, and burrowed shales (Cluff et al. 1981).

The upper part of the Selmier Shale may be equivalent to the lowermost part of the Sweetland Creek Shale in western Illinois, but most of the Sweetland Creek is younger than the Selmier (Cluff et al. 1981, p. 28). The Sweetland Creek consists of alternating beds of dark greenish gray, greenish gray, and grayish green shales that are indistinctly bedded and moderately bioturbated. Minor amounts of olive gray to olive black shales are thickly or poorly laminated and have few or no burrows.

The Sweetland Creek Shale of western and central Illinois interfingers with and grades laterally into the
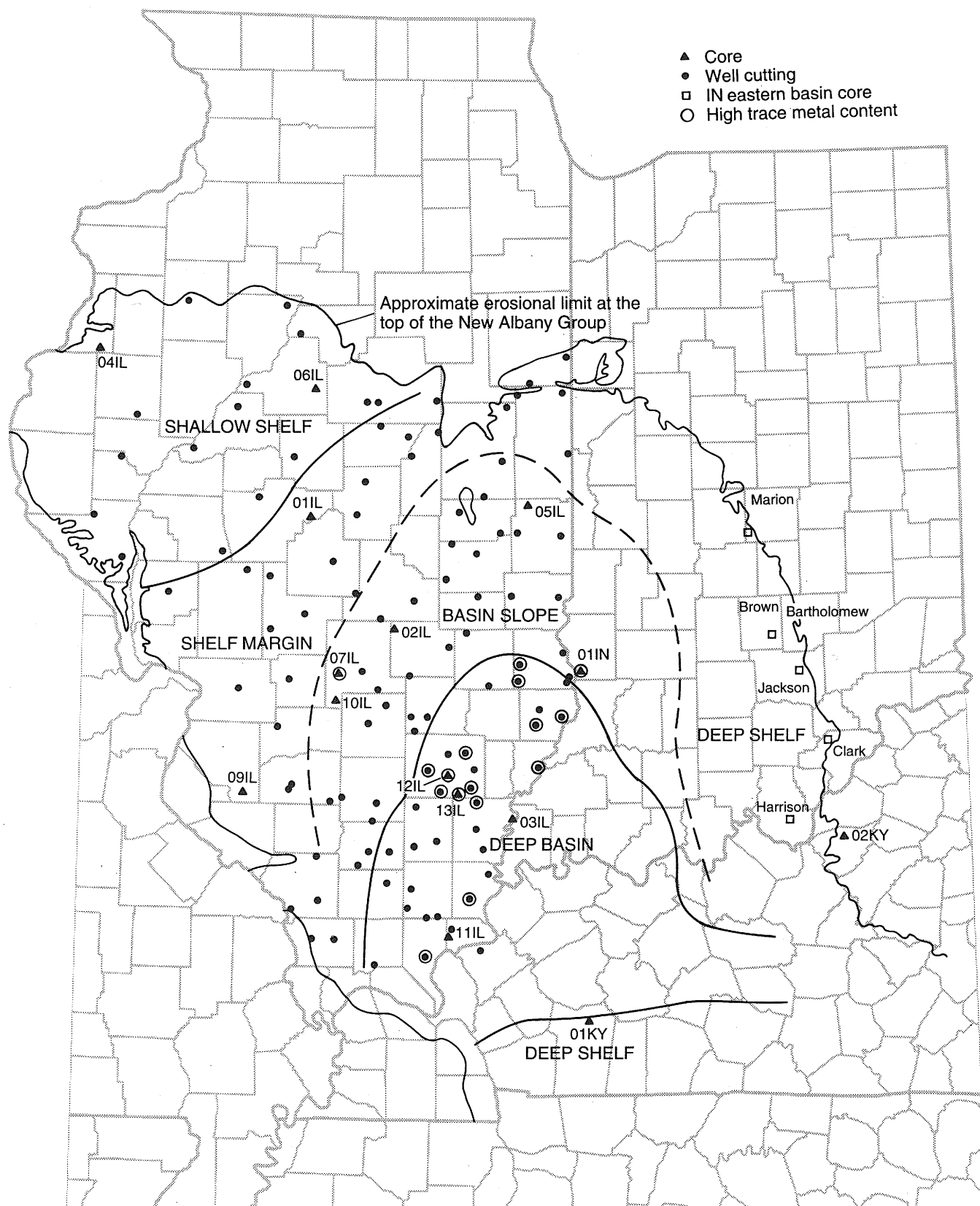
Figure 2 Map of the Illinois Basin with locations at which cores and well cuttings were sampled through the New Albany Group. Locations are reported in Bergstrom, Shimp, and Cluff (1980, p. 12–14). Paleogeographic boundaries are from Lineback (1980) and Devera and Hasenmueller (1991). Locations of Eastern Gas Shales Project (EGSP) cores in the eastern basin studied by Lechler et al. (1979), Shaffer et al. (1981), and Hailer et al. (1982) are denoted by □. Locations of deep basin Grassy Creek samples and of a Hannibal Shale sample (from 07IL) that have anomalously high trace metal contents are circled.
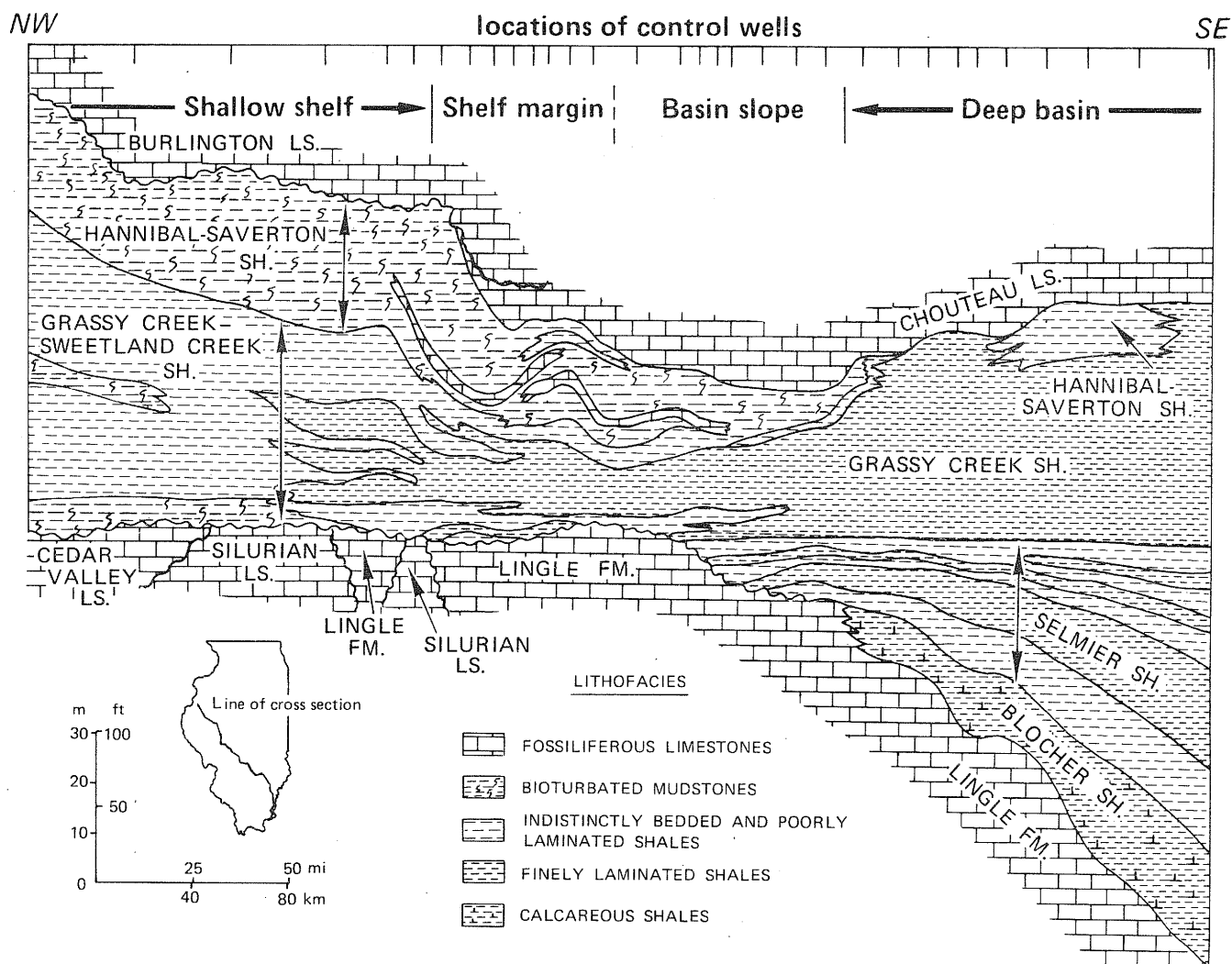
Figure 3 Generalized northwest–southeast stratigraphic cross section through the New Albany Group in Illinois (from Cluff, Reinbold, and Lineback 1981).

lower part of the Grassy Creek Shale of southeastern Illinois (fig. 3). Across much of western and north-central Illinois, the Sweetland Creek Shale is not consistently distinguishable from interfingering and overlying olive gray to olive black shales of the Grassy Creek that have thin interbeds of grayish olive green to grayish green shales. But in southern Illinois and western Kentucky, the Grassy Creek Shale is a sharply defined unit consisting of brownish black to grayish black, finely laminated, pyritic shales.

The topmost shale units, the Saverton and the Hannibal, are interbedded greenish gray and dark greenish gray shales. The units have some olive black beds. The greenish gray beds are nonlaminated and extensively burrowed. The Saverton and Hannibal are thickest in western and central Illinois and thin to the southeast.

On the eastern side of the basin, in south-central Indiana, the brownish black, calcareous Blocher Shale is overlain by the Selmier Shale (Hasenmueller and Woodard 1981). The upper part of the New Albany here consists of three members that are not always lithologically distinct. In ascending order, these are the Morgan Trail, Camp Run, and Clegg Creek Members. The last is a predominately brownish black, finely laminated, pyritic shale. These member names are also applied to the New Albany shale strata in north-central Kentucky. The Morgan Trail, Camp Run, and Clegg Creek Members are time equivalent to the Grassy Creek Shale in southeastern Illinois (Cluff et al. 1981).

In south-central and southeastern Indiana, several thin beds in the upper Clegg Creek Member (or base of the Ellsworth Member, where the Ellsworth Shale can be recognized) are formally recognized. In ascending order, these are (1) the Falling Run Bed: a 0.2-foot-thick interval of phosphate nodules; (2) the Underwood Bed: a thin, greenish gray shale of local extent; (3) the Henryville Bed: a 0.5- to 3.5-foot-thick, brownish black to black, pyritic shale with very high concentrations of organic carbon and trace metals; and (4) the Jacobs Chapel Bed: a thin, greenish gray, glauconitic shale (Hasenmueller and Woodard 1981, Hasenmueller and Leininger 1987).

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SAMPLES, ANALYTICAL METHODS, AND DATA

For the Eastern Gas Shales Project, almost 400 samples from the New Albany Group were analyzed for organic carbon and sulfur or pyritic sulfur, as well as for all other major and minor elements and for trace elements (Frost et al. 1985). Figure 2 shows the locations of the 15 cores from which 216 samples from the Blocher, Selmier, Sweetland Creek, Grassy Creek, Saverton, and Hannibal Formations were taken for analysis. In addition, 158 samples (labeled NAS-0nnn) of well cuttings from 110 locations (two were outcrops) provided coverage of most of the Illinois Basin within Illinois (fig. 2).

For the Eastern Gas Shales Project, samples were selected from the cores and well cuttings as follows. From each core, a 3- to 5-inch-long segment was taken at approximately 10-foot intervals through the New Albany Group, avoiding pyrite lenses more than 1 inch thick or any particularly bad fracture that would interfere with sawing out the segment (Harvey et al. 1977). The core segment was split vertically, and one-third of it was crushed and ground for chemical and other analyses. Sometimes from a 10-foot-long core section, an additional one or two segments were sawed and split to provide samples for mineralogic or lithologic study; these samples also were analyzed for chemical composition. One to four well cuttings samples were analysed from any one well; if possible, there was a sample from every 100 feet of depth and at least one sample from each formation. Each sample was picked from cuttings representing a 5- to 10-foot-depth interval. Care was taken to avoid any obvious caved material.

In the discussion of the carbon–sulfur–iron relationships in these shales, it is important to keep in mind that the samples were taken at wide intervals of depth. Thus, they do not provide a continuous or inclusive record of carbon, sulfur, and iron contents at each location through the formations of the New Albany Group.

Pyritic Sulfur Content

Pyritic sulfur concentrations were determined in the 216 core samples, but not enough material from the 158 well cuttings samples was available to do analyses for varieties of sulfur. Results for the core samples (Frost et al. 1985) showed that the sulfur is nearly all pyritic. Pyritic sulfur averaged 94% ± 6% (one standard deviation) of the total sulfur in all core samples. The percentage was highest in the freshly drilled cores and averaged 96% ± 4% in the samples from 11 cores drilled in the 1970s, compared to 84% ± 15% in 34 samples from 4 cores drilled before 1970. The proportion of sulfate sulfur was highest in samples from core 01IL, which had been stored in air since 1939. These results on the stored cores are consistent with the fact that pyrite undergoes some oxidation to sulfate in stored cores. Therefore, it was concluded that the amount of pyrite originally in well cuttings samples and old cores can be calculated more accurately using total sulfur content rather than the pyritic sulfur content that is now measured in a sample. In this report, therefore, total sulfur concentrations are used to represent pyritic sulfur.

Organic sulfur is ignored. Organic sulfur values were calculated as the small difference between total sulfur and the sum of the pyritic and sulfate sulfur values that were determined for 180 of the core samples by Frost et al. (1985). These organic sulfur values range from 0% to 0.6% and average <0.1%; they are, however, subject to large absolute analytical error. Dickerson (personal communication 1979, and Dickerson 1980) calculated an average organic sulfur content of 1.6 ± 0.3 weight % of the organic carbon content, based on elemental analysis of the benzene–methanol extracts from six core samples. This value may be lower than the true value because benzene–methanol extraction is not efficient for the sulfur-containing aromatic and aliphatic compounds with relatively high molecular weights. As measured, the organic sulfur is an insignificant part of the total sulfur and insignificant with respect to the pyritic sulfur content of these shale samples.

Degree of Pyritization of Iron and Determination of Reactive Iron

Elemental concentrations that had been determined in chemical analyses for the Eastern Gas Shales Project were used to calculate the proportion of the total iron residing in pyrite (DOP_T) for the samples for this report. DOP_T was calculated as the ratio of pyritic iron (calculated from total sulfur, assuming stoichiometric FeS_2) to total iron determined in each sample.

As previously discussed, the proportion of the total iron residing in pyrite may not reflect the fraction of the iron that could have formed pyrite. Some iron in sediments might occur in species that would not react with hydrogen sulfide to form pyrite (Berner 1970).

To test whether nonpyritic iron in the New Albany shale samples studied here would be available for formation of pyrite, 71 shale samples were taken for determination of HCl-soluble iron, according to the method of Berner (1970). Replicate 0.1 g portions of dried samples were boiled in 12 N HCl for 1 minute. The residue was filtered off and washed with distilled water. The HCl-leach solution was diluted to 50 ml with water. The reactive iron concentration was determined by atomic absorption spectrophotometry, and the resulting value was used to calculate the acid-soluble iron content of the shale sample (Appendix 1). The average mean error between replicates was 3.9% relative.

To check that values obtained for iron as determined by atomic absorption spectrophotometry are comparable to those obtained by X-ray fluorescence spectroscopy, the same 71 shales were analyzed for total iron by atomic absorption spectroscopy, using an acid-digestion procedure. Resulting values (Appendix 1) agreed with the total iron values obtained by X-ray

fluorescence analysis as reported in Frost et al. (1985), within 10% relative, and with random difference.

For the 71 samples, the proportion of reactive iron residing in pyrite (DOP_R) was calculated as the ratio of pyritic iron to the sum of the pyritic iron and hydrochloric acid-soluble iron concentrations. In many studies, only total iron in a shale is reported, so only DOP_T can be calculated. To evaluate what DOP_T can reveal about how iron controls pyrite formation in organic matter-rich shales, DOP_T values of New Albany shale samples were compared to the DOP_R values.

Lithofacies Classification

Lithofacies data from previous geologic studies of the New Albany Group for the Eastern Gas Shales Project provide independent information on the depositional history of these shales. Those studies used the stratified anoxic basin model of Rhoads and Morse (1971) and Byers (1977), which correlates the upper aerobic zone ($O_2 > 1.0$ mL/L) of a marine basin with shelly fauna and a rock record of fossiliferous limestones, an intermediate dysaerobic zone ($O_2 = 0.1$ to 1.0 mL/L) with bioturbated greenish gray mudstones, and a bottom anaerobic zone ($O_2 < 0.1$ mL/L) with laminated dark gray to black shales.

The lithofacies classification for the shales of the New Albany Group developed by Harvey et al. (1977), Cluff (1980), and Cluff et al. (1980) was based on radiography of shales and petrography of thin sections of samples from the cores. The specimens were classified according to five features as summarized in table 1. Because the lithofacies classification includes color (which is largely determined by organic carbon content) and pyrite occurrence, the lithofacies definitions do not describe depositional environments in a way that is completely independent of the information provided by the organic carbon and sulfur concentration data and the organic carbon–sulfur relationship in these shales. However, other parameters of the classification do indicate specific new aspects of a sedimentary environment.

At times during the formation of the New Albany Group, aerobic conditions (>1.0 mL O_2/L water) prevailed, and limestones and dolomites (for example, the Chouteau Limestone, fig. 3) formed in shallow-water environments (<50 m) that were locally high in energy (Cluff et al. 1980). But most of the time, oxygen levels were lower. Then the shales of the New Albany Group were formed in depositional environments inferred from the four lithofacies types:

Table 1   Lithofacies characteristics for shales of the New Albany Group (after Harvey et al. 1977 and Cluff et al. 1980).

	I Highly bioturbated mudstones	II Indistinctly bedded shales	III Thickly laminated shales	IV Finely laminated shales
Color				
gray or brownish gray	O			
greenish gray	X			
olive gray		X		
olive black		O	X	
brownish black			O	X
Bedding and lamination				
massive	X			
indistinctly bedded		X		
thickly or poorly laminated		O	X	
finely laminated			O	X
Bioturbation				
very extensive or total	X			
extensive		X		
moderate		X	O	
sporadic			X	
Pyrite form				
fine hair-like features (burrows?)	X	X		
large burrow fillings		X	O	
nodules		O	X	X
laminae			X	X
Spores	absent	rare	common	major

X = major or common   O = minor or rare

Lithofacies I Bioturbated mudstones: dysaerobic (0.1 to 1.0 mL O_2/L water), moderately deep (50–150 m?), quiet water environments.

Lithofacies II Indistinctly bedded shales: marginal dysaerobic to anaerobic (<0.1 mL O_2/L water), moderate to deep (150 m or greater?), quiet water environments.

Lithofacies III Thickly laminated shales: anaerobic, deep (>150 m?), quiet water environment, broken only by occasional currents.

Lithofacies IV Finely laminated shales: anaerobic, deep, very quiet water environments.

The succession from lithofacies I to IV indicates qualitatively increasingly anaerobic conditions.

RESULTS AND DISCUSSION

Organic Carbon to Sulfur Relationship

The organic carbon and total sulfur contents for all the New Albany shale samples are plotted in figure 4, except that samples from the Hardin County core 11IL that would plot in figure 4A are shown in figure 7. Most of the samples (fig. 4A) show a general positive correlation between organic carbon and sulfur. These samples plot near a line characterized by C/S = 2.8, which is the value typical for sediments from modern normal marine environments (Goldhaber and Kaplan 1974). The few remaining samples (fig. 4B) have a much higher or lower C/S ratio. Reasons for this scatter will be discussed below.

Figure 5 shows the relationship between sulfur and organic carbon content for core samples identified according to lithofacies interpretations made by Harvey et al. (1977), Bergstrom and Shimp (1978a, 1978b, 1979), and R.D. Harvey (personal communication 1987). The plot and the values in table 2 indicate that organic carbon content generally increases with increasingly anoxic conditions (as determined from lithofacies interpretation), although there is considerable overlap of points in one lithofacies type group with those in another.

In figure 5, there are samples with carbon and sulfur values that plot in the field occupied by samples from the euxinic Black Sea (Leventhal 1983, fig. 1); that is, the points are above the line (shown) drawn by Leventhal (1987) to separate sediments of euxinic environments (data of Hirst 1974) from sediments of normal marine environments (data of Goldhaber and Kaplan 1974). Some of these samples that plot above the line are low-carbon content samples of lithofacies I and II, and some are bioturbated samples of lithofacies III. For example, the lithologic description of the sample (S00174, 05IL01L3) with 5.0% organic carbon and 3.5% sulfur, in figures 4A and 5B, indicates that it is from a thin, bioturbated bed with massive laminations and abundant pyrite nodules 3 to 7 mm in diameter distributed in burrows (Bergstrom and Shimp 1978a). The sample in figure 4A (S00021, 01IL10L1) with 1.3% organic carbon and 2.4% sulfur is of lithofacies type II (fig. 5B). Moreover, the pyrite in the sample had a positive δ^{34}S, which indicates sulfide formation from a limited reservoir of sulfate (Anderson et al. 1987). Samples such as these indicate that sediment was deposited in at least partially oxygenated bottom waters and that pyrite formed under reducing conditions that subsequently developed in the sediments, as well as that some pyrite was formed in a later stage of diagenesis.

The extrapolation of the calculated linear regression of sulfur on carbon for various groups of samples gives a positive intercept on the sulfur axis (table 2). To test whether this result indicates euxinic conditions in the depositional environment, as Leventhal (1983) reported, the samples from core 06IL were evaluated.

The samples from core 06IL (fig. 6A) show a strong correlation of sulfur with organic carbon, except for one sample that has unusually high sulfur and iron contents. Excluding that sample, the 10 samples with organic carbon contents greater than 2.5% exhibit a correlation with an average C/S value of 2.4. Nineteen samples with relatively low organic carbon content (<2%) have an average C/S value of 1.4, and their preponderance results in a low mean C/S value of 1.7 for the core (table 2). The sulfur–carbon covariance in samples from 06IL is well fitted by a parabola drawn through the data points to the origin (fig. 6A). But, when the data are fitted to a linear regression, the samples with low organic carbon content and low C/S ratios contribute significantly to causing the positive intercept of 0.45 on the sulfur axis (table 2). However, the samples with organic carbon content <2% are mainly of lithofacies type II: indistinctly bedded, bioturbated sediments with pyrite-filled burrows (table 1). These characteristics indicate that the pyrite in these samples formed later in diagenesis after the sediment was depleted of oxygen. The fact that pyrite can form at several stages during sedimentation and diagenesis complicates the interpretation of the positive y-axis intercept of the sulfur on carbon regression. The carbon-sulfur pattern shown by the samples from core 06IL applies to the other groups that contain many samples with low organic carbon content: core 04IL (mean C/S = 1.8 for 30 samples [table 2]), the group of 60 samples from the Saverton and Hannibal Formations (mean C/S = 2.2 [table 2]), the lithofacies I and II groups, and the shallow shelf group (table 2). The higher level of sulfur relative to carbon in these samples may be due to one or more of the following factors: (1) the rate of sedimentation differs, (2) the samples reflect a source of organic matter different from that in organic matter-rich samples in the deep basin, (3) aerobic destruction of organic matter is greater if the environment cycled between aerobic and dysaerobic and the sediment was reworked by the burrowing and scavenging activities of benthic organisms, or (4) a small part of the total iron may have been highly reactive so that iron sulfide initially formed easily and rapidly.
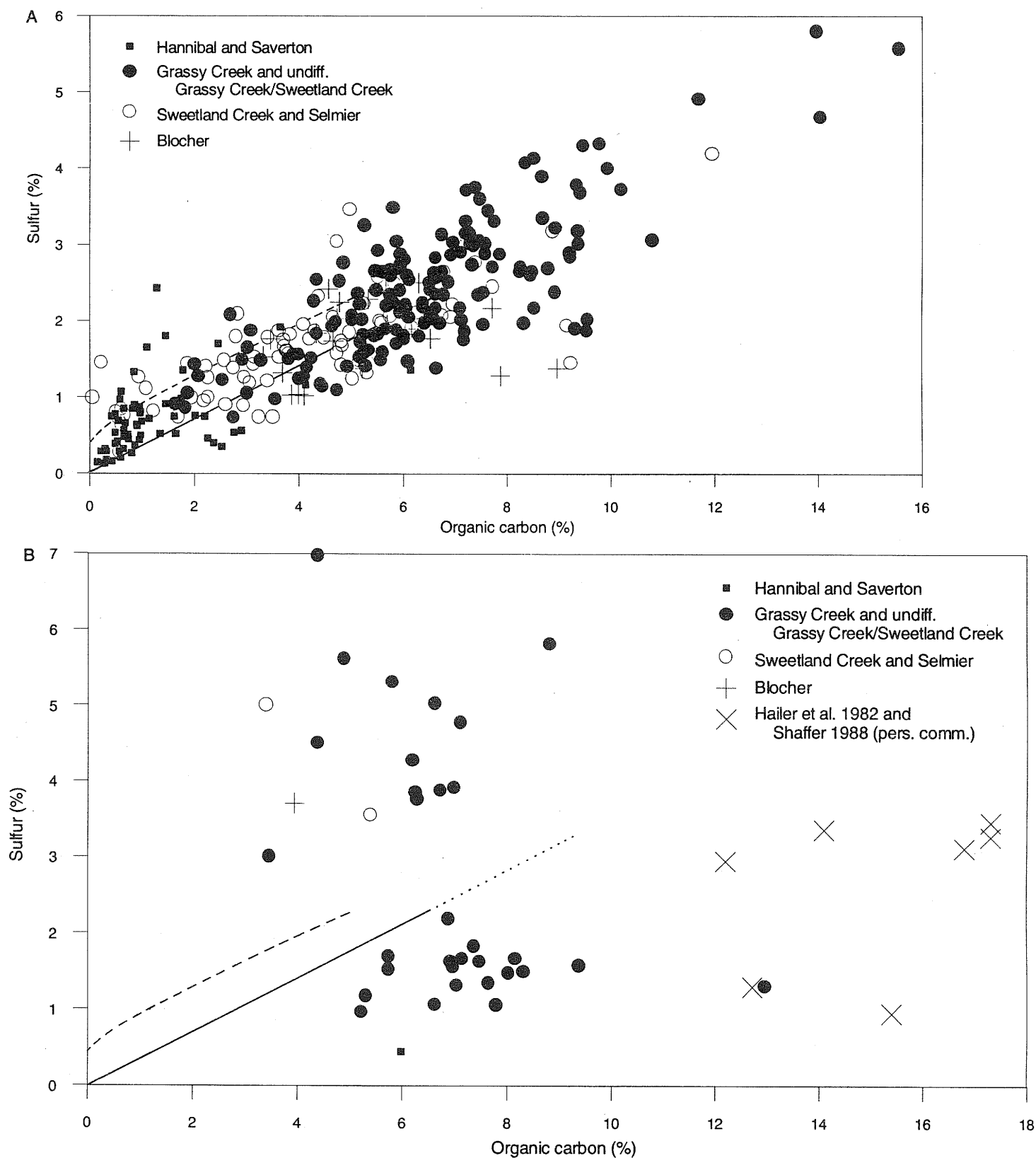
Figure 4 Variation of sulfur with organic carbon content in 350 shale samples from the different formations of the New Albany Group in the Illinois Basin. The straight line is the regression line (C/S = 2.8) for modern normal marine sediments. The dashed line is that drawn by Leventhal (1987) as representing the separation between sediments from euxinic and modern normal marine environments. (A) Most of the samples plot in the field about the regression line of C/S = 2.8. Samples from core 11IL in Hardin County, Illinois, that would plot in this field are shown in figure 7. (B) A few samples tend to very high or low organic carbon to sulfur ratios. Also plotted, from Hailer et al. (1982) and N.R. Shaffer (personal comm. 1988), are data from seven samples from the top 10 feet of the New Albany (the Clegg Creek) in cores from Marion, Brown, Jackson, Clark, and Harrison Counties in southeastern Indiana and in the core from Sullivan County in southwestern Indiana.

Table 2 Mean organic carbon, sulfur and iron concentrations, and related data, in project samples by formation, lithofacies (definitions in text), core, and region.

Group	No. of Samples	Mean value ± σ (%)					Regression of S on Org. C				Regression of DOP_T on Org. C				Regression of Fe on Org. C			
		Org. C	Total S	Fe	Org. C / Total S	DOP_T	Slope	Inter-cept (%)	Corr. coeff.	Signif.	Slope	Inter-cept (%)	Corr. coeff.	Signif.	Slope	Inter-cept (%)	Corr. coeff.	Signif.
by formation**																		
HBSV	60	1.3±1.2	0.73±0.48	3.5±0.7	2.2±2.1	0.18±0.10	0.14	0.55	0.35[1]	+[2]	0.028	0.14	0.35	+	0.095	3.32	0.18	
Grassy Creek	189	6.5±2.2	2.5±1.1	4.1±0.8	2.9±1.2	0.52±0.15	0.24	0.91	0.48	+	0.037	0.27	0.53	+	0.089	3.50	0.23	+
SDCK & SELM	101	3.7±2.3	1.7±0.8	3.6±0.7	2.2±1.1	0.40±0.15	0.23	0.83	0.67	+	0.049	0.22	0.74	+	0.040	3.45	0.13	
Blocher	24	5.3±1.5	1.9±0.6	2.3±0.7	3.0±1.3	0.73±0.13	0.049	1.7	0.11		-0.01	0.78	-0.11		0.11	1.75	0.22	
Blocher[a]	24	7.2±1.7	2.6±0.8	3.1±0.8	3.0±1.3	0.73±0.13	-0.036	2.8	-0.07		-0.002	0.74	-0.02		-0.035	3.35	-0.07	+
by lithofacies (core samples, excluding Blocher and core 11IL)																		
I[b]	18	0.65±0.34	0.61±0.37	2.8±0.7	1.4±1.1	0.19±0.10	0.64	0.19	0.58	*	0.20	0.06	0.68	+	0.44	2.48	0.22	
II	46	2.4±2.2	1.1±0.8	3.5±0.5	2.2±1.4	0.27±0.18	0.27	0.45	0.76	+	0.067	0.11	0.80	+	-0.007	3.54	-0.03	
III	58	4.6±2.6	1.8±1.2	3.8±0.9	2.9±1.9	0.39±0.19	0.24	0.67	0.51	+	0.054	0.15	0.73	+	-0.003	3.83	-0.0	
IV	54	7.4±3.0	2.8±1.3	4.4±0.9	2.9±1.5	0.55±0.17	0.25	0.98	0.59	+	0.034	0.30	0.60	+	0.11	3.53	0.39	+
by core																		
04IL	32	1.5±1.2	0.93±0.42	3.5±0.5	1.7±1.1	0.23±0.09	0.14	0.71	0.41	*	0.016	0.20	0.21		0.23	3.20	0.56	+
04IL[c]	30	1.6±1.2	0.91±0.42	3.6±0.5	1.8±1.1	0.22±0.08	0.18	0.63	0.50	+	0.029	0.17	0.44	+	0.19	3.28	0.51	+
06IL	30	2.4±2.4	1.3±1.1	4.0±0.6	1.7±0.8	0.27±0.18	0.37	0.44	0.78	+	0.061	0.13	0.82	+	0.14	3.67	0.53	+
06IL[d]	29	2.3±2.4	1.2±0.8	3.9±0.5	1.7±0.8	0.25±0.15	0.32	0.45	0.92	+	0.055	0.13	0.86	+	0.11	3.68	0.53	+
01IL	19	3.0±2.8	1.2±1.0	3.2±0.9	2.6±1.5	0.29±0.19	0.27	0.36	0.80	+	0.053	0.13	0.76	+	0.22	2.52	0.68	+
07IL	6	3.9±2.4	1.4±1.5	3.4±0.9	4.9±4.7	0.31±0.27	0.41	-0.16	0.66	*	0.070	0.04	0.64	+	0.27	2.35	0.75	+
07IL[e]	5	3.5±2.5	1.6±1.6	3.4±1.0	3.2±2.3	0.35±0.28	0.59	-0.44	0.92	*	0.10	-0.01	0.94	+	0.33	2.27	0.82	+
02IL	11	5.4±2.8	1.9±1.1	4.1±0.7	3.0±1.1	0.39±0.17	0.35	0.04	0.90	+	0.055	0.09	0.92	+	0.20	2.95	0.85	+
02KY[f]	8	8.3±4.2	3.7±2.1	4.7±1.6	2.6±1.2	0.64±0.15	0.20	2.05	0.40		0.016	0.51	0.48	+	0.14	3.48	0.38	
02KY[g]	7	8.9±4.2	3.2±1.7	4.3±1.4	2.9±1.0	0.61±0.13	0.36	-0.03	0.90	+	0.028	0.37	0.91	+	0.27	1.93	0.83	+
01KY[h]	14	6.8±3.7	2.7±1.7	3.5±1.4	2.8±1.4	0.64±0.22	0.29	0.74	0.64	*	0.047	0.32	0.79	+	0.14	2.50	0.38	
01KY[i]	12	6.9±4.0	2.3±1.4	3.1±1.0	3.1±1.3	0.62±0.23	0.31	0.15	0.89	+	0.048	0.28	0.84	+	0.17	1.93	0.65	+
01IN[j]	22	6.8±3.1	2.4±1.0	4.2±0.7	3.0±1.9	0.49±0.14	0.21	0.97	0.62	+	0.032	0.27	0.70	+	0.044	3.89	0.19	
01IN[k]	21	6.5±2.9	2.4±1.0	4.2±0.7	2.7±1.0	0.49±0.14	0.30	0.49	0.83	+	0.044	0.20	0.89	+	0.091	3.64	0.36	
01IN[l]	20	6.8±2.6	2.5±1.0	4.2±0.7	2.8±0.9	0.51±0.12	0.31	0.42	0.80	+	0.041	0.23	0.86	+	0.15	3.13	0.56	*
13IL[m]	21	5.6±2.3	2.2±1.2	3.9±0.9	2.8±1.4	0.48±0.17	0.34	0.36	0.62	+	0.051	0.20	0.70	+	0.18	2.84	0.47	
03IL[n]	5	4.8±3.9	1.6±1.4	3.4±1.0	3.1±1.2	0.37±0.22	0.32	0.04	0.93	*	0.050	0.12	0.89	*	0.23	2.23	0.96	+
11IL[o]	25	2.7±1.9	1.7±1.0	3.8±0.8	1.6±0.9	0.39±0.19	0.31	0.88	0.59	+	0.072	0.20	0.72	+	-0.013	3.78	-0.03	
11IL	24	2.6±1.9	1.6±0.7	3.6±0.6	1.6±0.9	0.38±0.18	0.29	0.83	0.73	+	0.070	0.20	0.74	+	-0.036	3.74	-0.11	
NAS[p]	147	5.7±1.9	2.2±0.8	3.9±0.7	2.8±1.0	0.48±0.15	0.25	0.71	0.58	+	0.051	0.19	0.65	+	0.060	3.55	0.17	*
by region (excluding Blocher)																		
Shallow shelf	81	2.4±2.1	1.2±0.9	3.8±0.6	1.9±1.1	0.26±0.14	0.29	0.49	0.74	+	0.047	0.15	0.72	+	0.16	3.44	0.61	+
Shelf margin	49	4.7±2.8	1.7±1.0	3.7±1.0	2.9±1.2	0.37±0.16	0.26	0.49	0.72	+	0.042	0.17	0.76	+	0.22	2.74	0.62	+
Basin slope	90	6.3±2.6	2.4±1.1	4.1±0.8	2.9±1.7	0.50±0.16	0.26	0.80	0.59	+	0.038	0.25	0.63	+	0.12	3.38	0.39	+
Deep basin	130	5.3±2.5	2.2±1.1	3.7±0.8	2.6±1.3	0.51±0.18	0.25	0.82	0.60	+	0.050	0.24	0.71	+	0.058	3.34	0.18	*

**HBSV = Hannibal and Saverton, SDCK & SELM = Sweetland Creek and Selmier

[1] r(S, Org. C) = 0.45 and r(DOP_T, Org. C) = 0.46 if the metal-rich sample S00127 (Table 3) is omitted

[2] + significant at the 99% level of confidence; * significant at the 95% level of confidence

[a] On carbonate-free basis

[b] Excluding S00161 with Org. C = 0.06%

[c] Excluding S00161 with Org. C = 0.06% and S00162 with Org.C = 0.22%

[d] Excluding S00168 with Fe = 6.2%, S = 5.6%

[e] Excluding anomalously metal-rich S00127

[f] Blocher excluded

[g] Also excluding S00398 with Fe = 7.1%, S = 7.0%

[h] 4 Blocher excluded

[i] Also excluding S00005 with Fe = 6.6%, S = 5.3% and S00003 with Fe = 5.0%, S = 5.0%

[j] 3 Blocher excluded

[k] Also excluding anomalously metal-rich S00127

[l] Also excluding high carbonate S00369

[m] 3 Blocher excluded

[n] 2 Blocher excluded

[o] Excluding S00346 with Fe = 6.3%, S = 5.0%

[p] 11 Blocher excluded
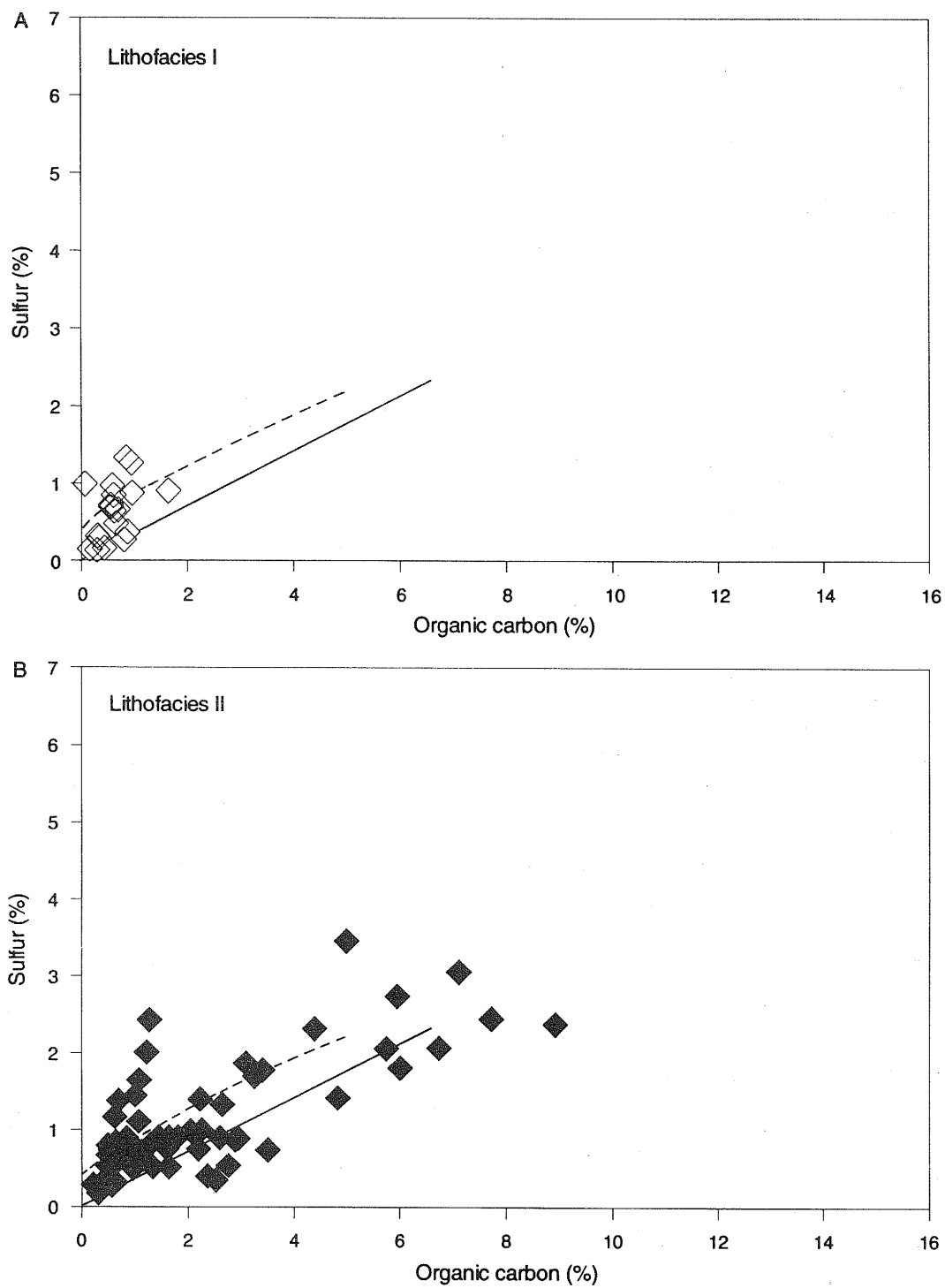
Figure 5 Variation of sulfur with organic carbon content in samples classified according to lithofacies type from cores through the New Albany Group in the Illinois Basin. The straight line is the C/S = 2.8 regression line, and the dashed line is Leventhal's separation of euxinic and modern normal marine sediments.
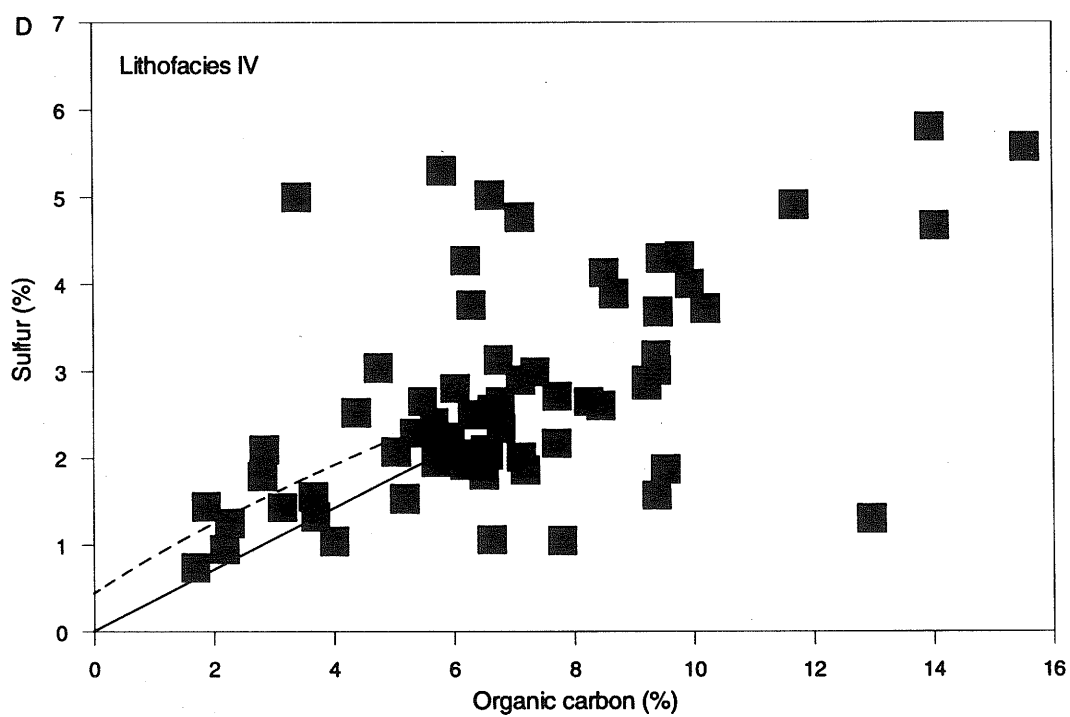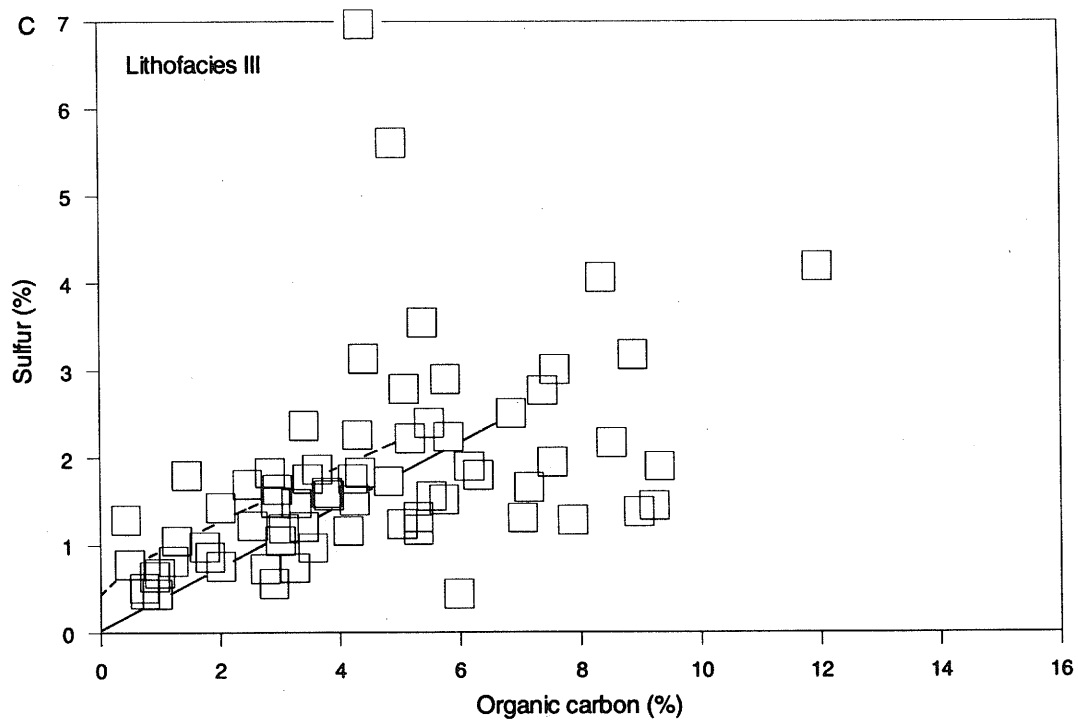
Figure 5   continued.

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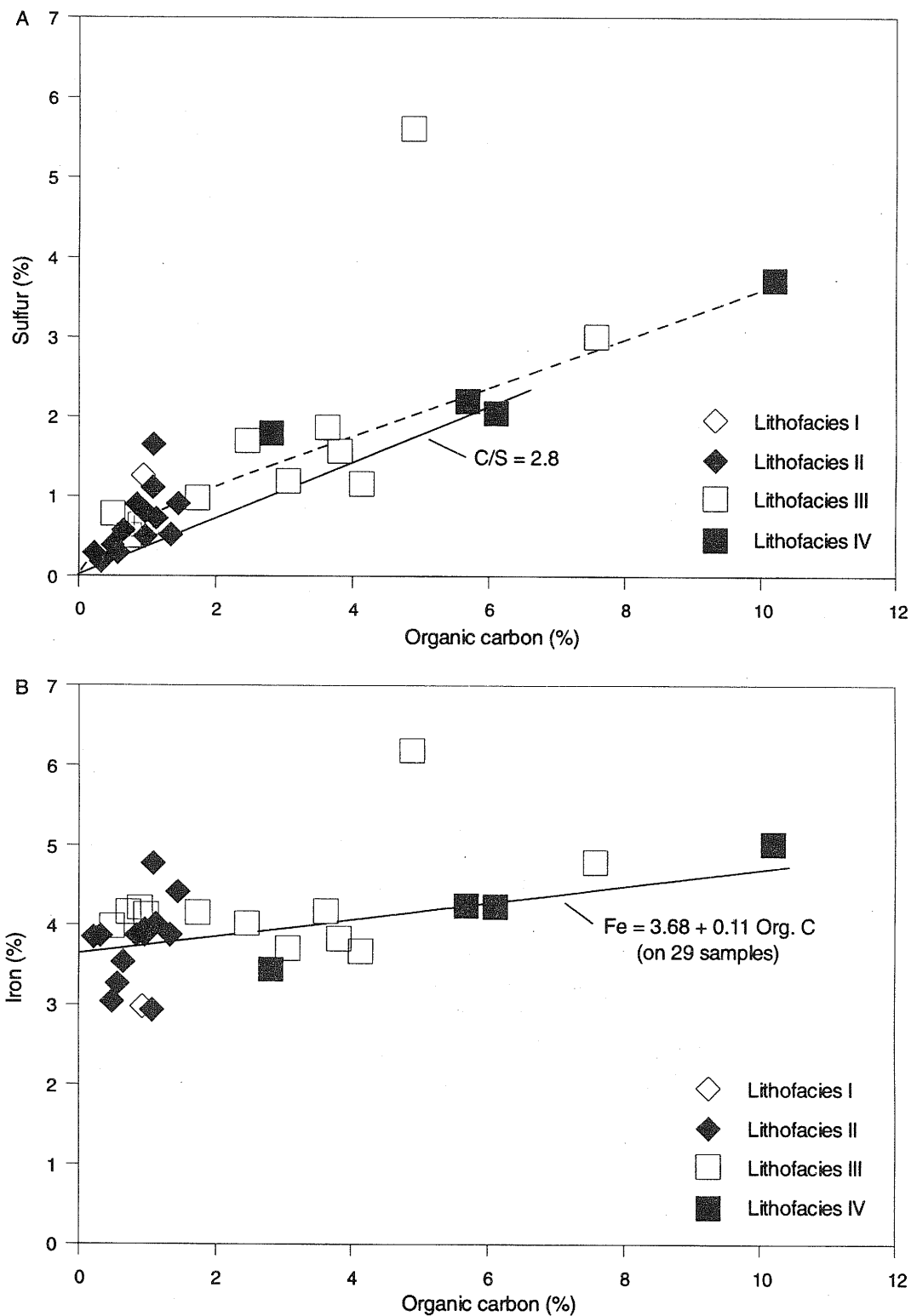
Figure 6 Variation with organic carbon of (A) sulfur and (B) iron content in samples, classified according to lithofacies type, of New Albany Group shale from the Tazewell County, Illinois, (06IL) core. In (A) the data (excepting one datum with S = 5.6%) are fitted by the dashed curve whose function is $y = 0.72\,x^{0.66}$ for organic carbon = 0.3% to 5%.
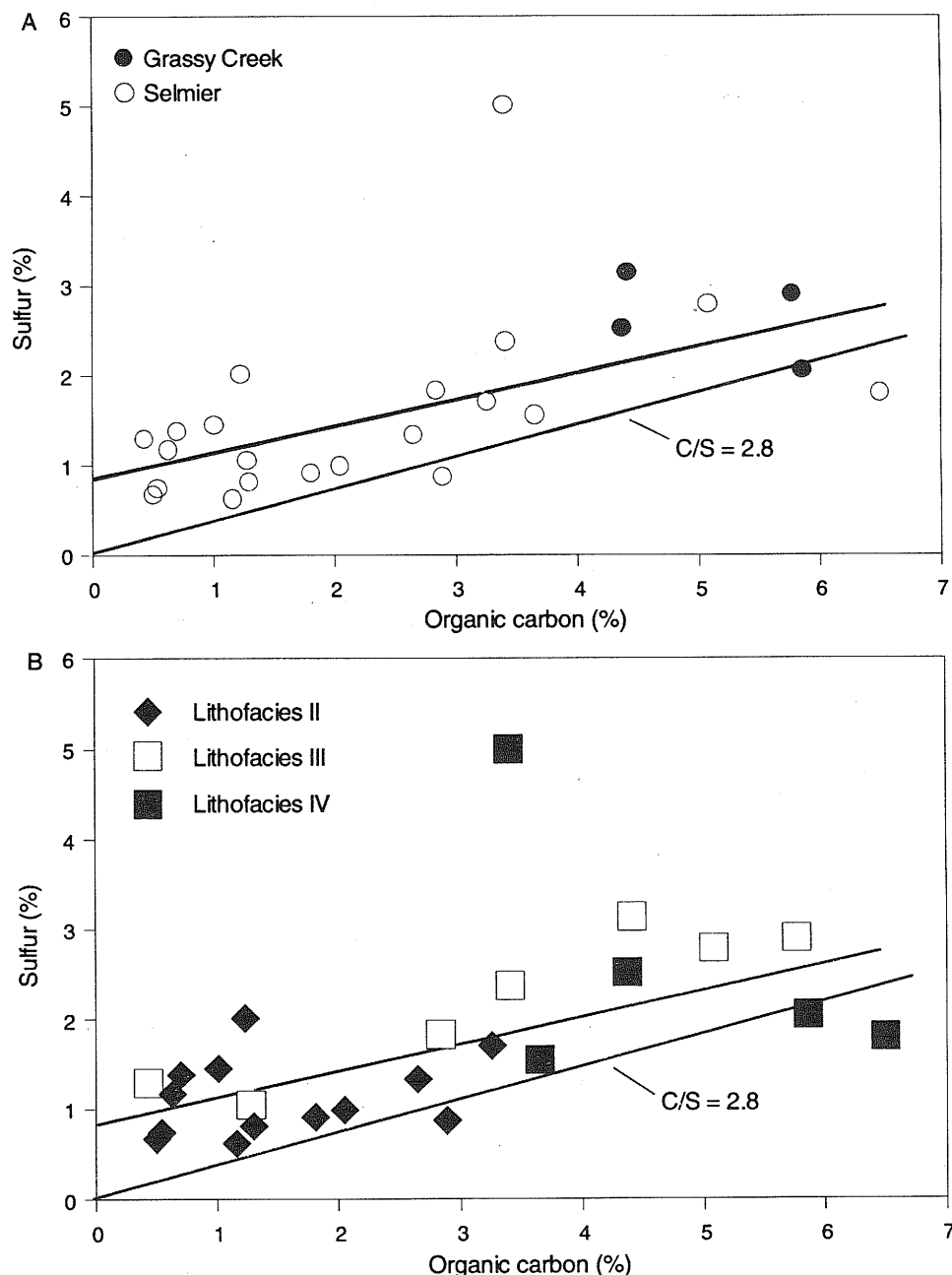
Figure 7 Variation of sulfur with organic carbon content in 25 samples from a core (11IL) from Hardin County, Illinois. The samples are identified (A) by formation and (B) by lithofacies type. The regression equation is S = 0.83 + 0.29 organic carbon.

Groups of samples in which most of the samples contain more than 2.5% carbon are the Grassy Creek Shale, the Blocher Shale, the samples from each of the shelf margin, basin slope, and deep basin regions, and the samples from each of the cores from those regions. These groups have higher C/S ratios than those of the low organic-carbon sample groups discussed above (table 2), with mean C/S values of 2.8 ± 0.4. Excluding a few anomalous samples (the samples footnoted in table 2 and plotted in fig. 4B) and with the exception of the Blocher Shale, all sample groups show a significant correlation of sulfur to carbon concentrations. Lithofacies and carbon–sulfur relationships for the Illinois Basin samples are consistent with a depositional environment where bottom waters are dysaerobic in shallow water (where organic-poor sediments are deposited) and become increasingly anoxic in quiescent deeper water (where an abundance of organic matter is produced and increasingly preserved). Iron–sulfur and carbon–DOP relationships may elucidate in more detail the paleoenvironmental conditions in various regions.

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In table 2, the high intercept (0.83) from the regression of sulfur on carbon for the samples from core 11IL, Hardin County, Illinois (fig. 7A), requires an explanation different from that advanced for the other cores discussed above. These samples have a wide range of organic carbon contents (0.4% to 6.5%), a change to a more anoxic lithofacies type with increasing organic carbon content, and a positive correlation of sulfur and DOP_T with organic carbon content (table 2). However, the samples have a low organic carbon to sulfur ratio (mean 1.6 ± 0.9) over the entire range of organic carbon content, thus giving a high intercept. The extra pyrite is particularly evident (fig. 7B) in a few samples with <1.3% organic carbon content that are of lithofacies II classification. The low C/S ratio may be due not to extra diagenetic pyrite but to a loss of organic carbon. Relatively high temperatures associated with subsequent igneous intrusions reported from the Hicks Dome area where this core was taken may have caused degradation of organic material and loss of volatile components. Evidence for thermal effects on the New Albany shales (depth interval 0 to 261 ft) in core 11IL includes negligible release of gas from the core (Dickerson and Chou 1980), a high vitrinite reflectance gradient for this core (Barrows et al. 1980), a lower hydrogen to carbon ratio in bitumens in samples from this core than was observed in the other cores (D.R. Dickerson, personal communication; Frost et al. 1985, p. 17) and a high degree of crystallinity of illite in samples from this core (Harvey et al. 1980).

Iron, DOP_R and DOP_T, and Organic Carbon Relationships

The DOP_R values for 52 samples analyzed for HCl-soluble iron are plotted against their organic carbon contents in figure 8. Values of HCl-soluble iron were determined and DOP_R calculated for an additional 19 samples from a group of metal-rich samples (fig. 10C). The Blocher Shale samples, which are high in carbonate, are excluded from the following discussion of figure 8. The strong correlation of DOP_R with organic carbon at low levels of organic carbon (<3%) is associated with the correlation of pyritic sulfur with organic carbon content (fig. 4A) and indicates that formation of pyrite was controlled mainly by the availability of reactive organic carbon for bacterial sulfate reduction.

At higher levels of organic carbon content (>3%), as organic carbon increases, DOP_R continues to increase, but with great variability, although the correlation between the two parameters remains significant at the 99% confidence level. Some of the variability is due to the wide range in total iron content of these shales, which is independent of organic carbon content. This variation is shown, for example, by the range in iron contents of several samples with about 1% organic carbon content in figure 6B. A wide variation in the detrital iron minerals and clay-adsorbed iron oxide contents of sediment can be due to (1) changes in the source material, (2) the grain size of the sediments, (3) the rate of production of organic matter, and (4) the
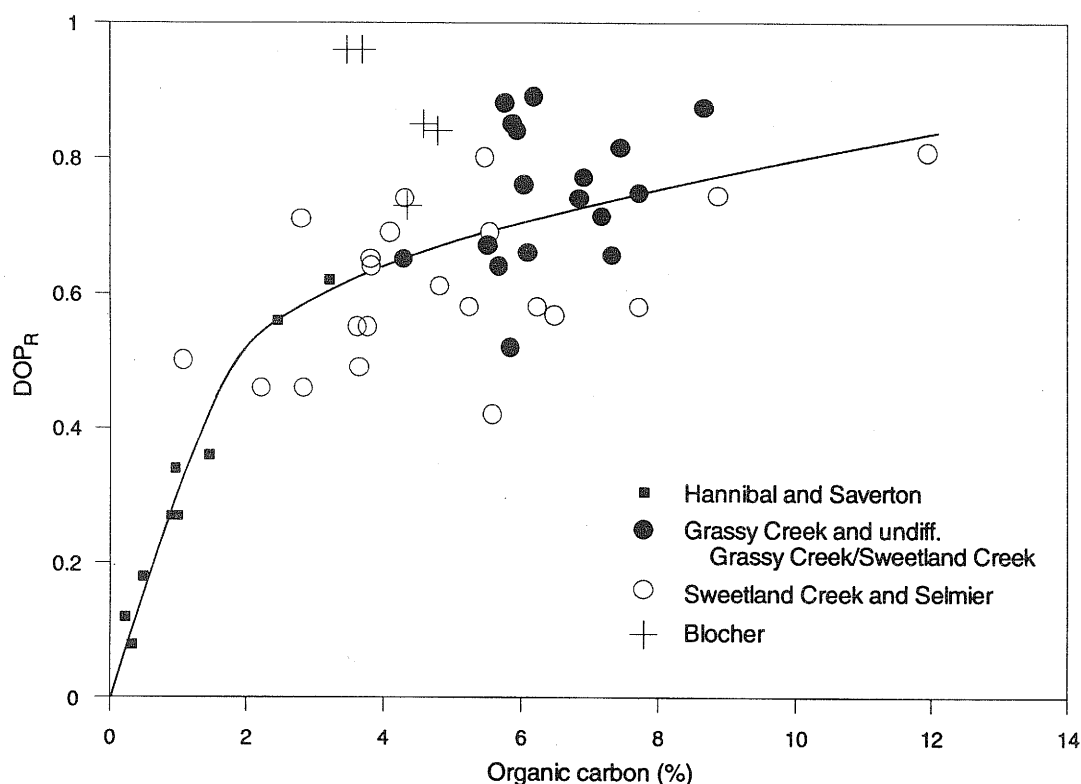

Figure 8   Variation of DOP_R with organic carbon content in 52 New Albany Group shale samples classified by formation. The Blocher samples were excluded from the data fitted by the curve.

rate of deposition of clastic sediments compared with the rate of deposition of organic matter.

Samples from core 06IL also show a slight, but significant, increase in iron content with increasing carbon content (fig. 6B). The correlation between iron and organic carbon content is not significant for all groups of samples as grouped by core, formation, or lithofacies type (table 2). Hence, it is inferred that the main source of iron in the shale is detrital material or iron adsorbed on the clays (Goldhaber and Kaplan 1974). Adsorption of colloidal hydrous ferric oxide onto, or reduction and complexation by, organic material provides supplementary means of accumulating or holding reactive iron.

The data points for the 71 New Albany shale samples that were analyzed for reactive iron are scattered about the line of correlation between DOP_R and DOP_T (fig. 9). This scatter of data points suggests that some variable amount of the total iron was never available to form pyrite. Therefore, the calculation of DOP_T does not give reliable information about the control by iron on pyrite formation. At higher levels of DOP_T (fig. 9) and organic carbon (fig. 8), the rate of increase in DOP_R slows, and DOP_R no longer approaches 1, which may indicate that the concentrated HCl treatment overesti-

mates the amount of reactive iron (Middelburg 1991). The DOP_R values greater than 0.85 (corresponding to DOP_T values greater than about 0.7) probably represent New Albany shale that lacks significant remaining reactive iron. That is, these DOP_R values represent samples that are iron-limited with respect to pyrite formation. This representation compares with an average for DOP_R of 0.84 in two systems where Raiswell and Berner (1985) concluded that pyrite formation was iron-limited: the Lower Jurassic Jet Rock of northeast England and the Lower Jurassic Posidonia Shales of southern Germany.

Many samples, mostly from the Grassy Creek Shale, have relatively high organic carbon content and DOP_T is >0.7 (see range of DOP_T in table 2) and no longer correlates with organic carbon content. The upper limit of reactive iron needed for pyrite formation apparently was reached in many of these samples. This iron limitation on pyrite formation explains why some samples with high organic carbon content (> ~7%) show no increase in sulfur content (fig. 4).

It is apparent from figure 8 that pyrite formation should be iron-limited in samples with very high organic carbon content. Hence it is surprising that a correlation between sulfur and organic carbon is main-
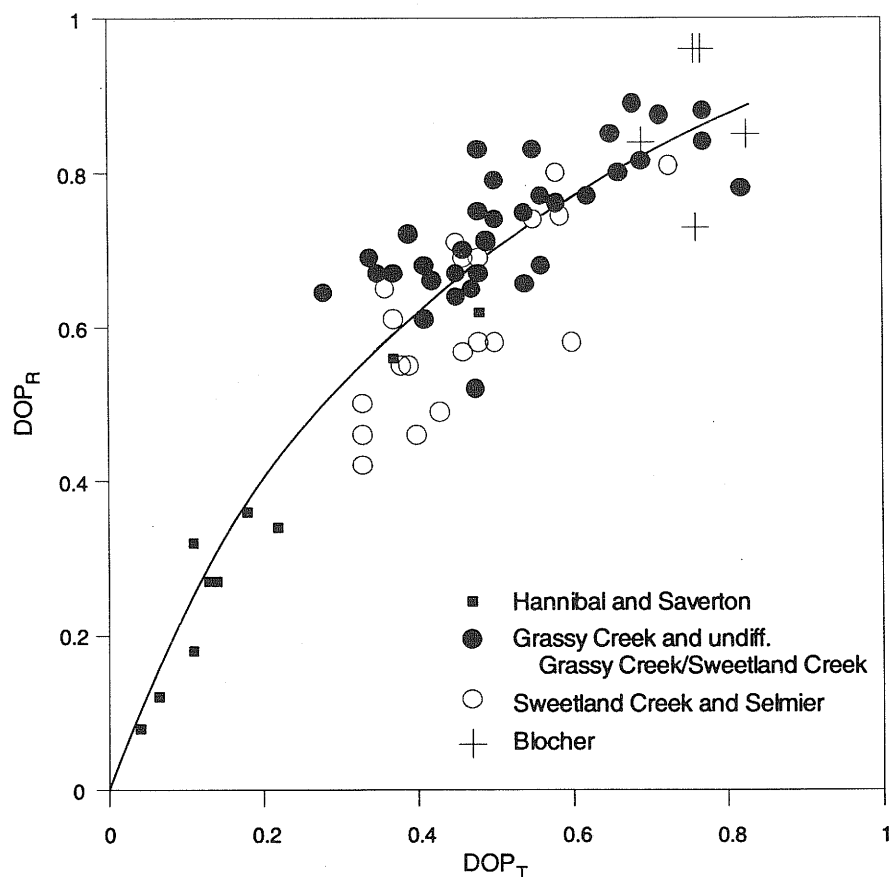
Figure 9 Comparison of degree of pyritization, DOP_T, calculated as the ratio of iron in pyrite to total iron in the sample with degree of pyritization, DOP_R, as measured by the ratio of iron in pyrite to the sum of iron in pyrite plus HCl-soluble iron in 71 New Albany shale samples.
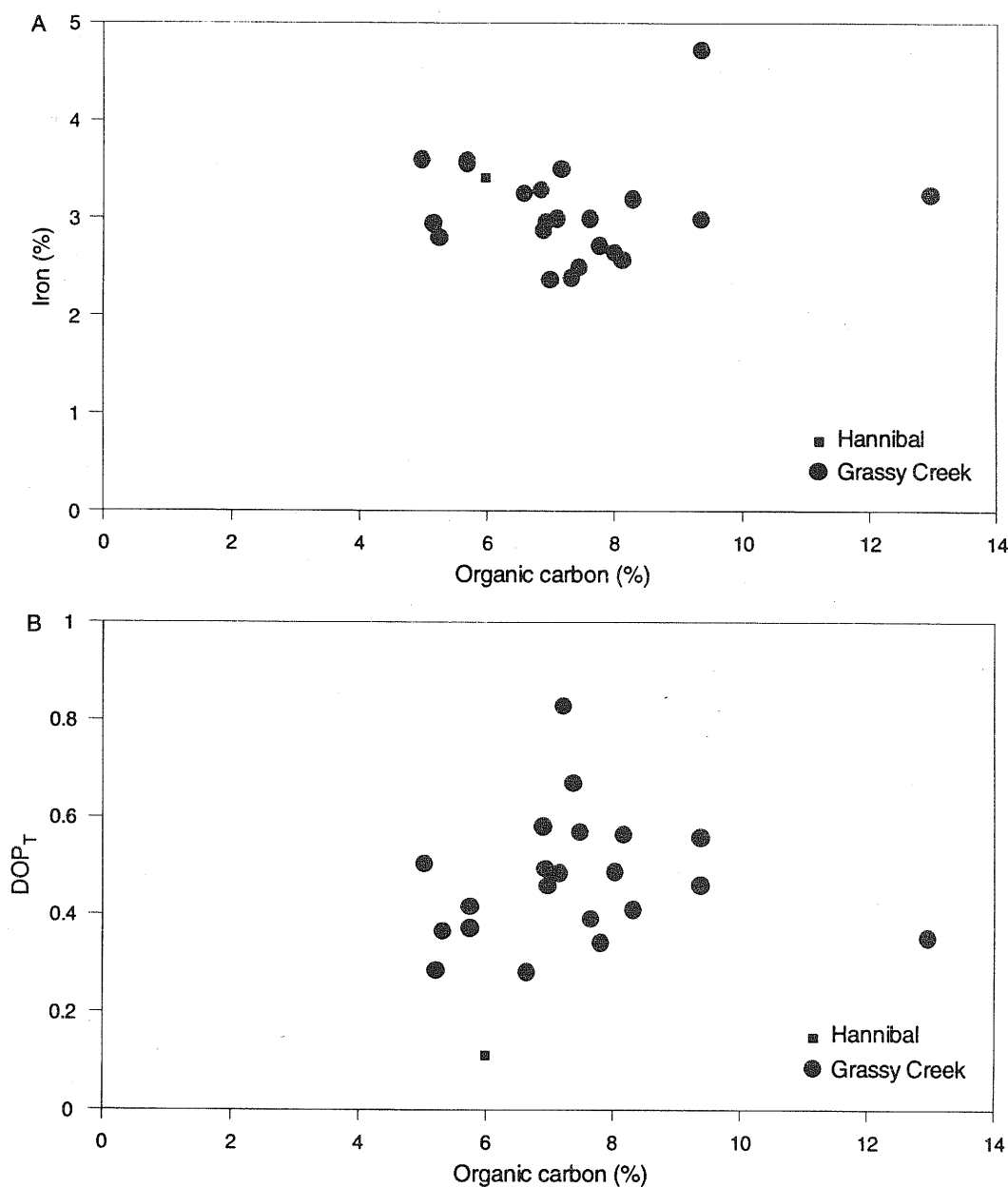
Figure 10   Variation of (A) iron, (B) DOP_T, and (C) DOP_R (18 of the samples) with organic carbon content in 22 samples of Grassy Creek Shale that have unusually high trace metals content. Samples are from the upper part of the Grassy Creek from 15 locations in the deep basin. Also plotted is Hannibal Shale sample 07IL01L2 (S00127) that has the same type of high trace metals content.

tained for some shale samples with organic carbon content as high as 15.5% (fig. 4A) and in samples with organic carbon contents as high as 14% from several cores from south-central Indiana (Hailer et al. 1982). This pattern of high organic carbon–sulfur correlation may be an artifact arising from the fact that in the set there are too few samples high in organic carbon content. To the extent that it is real, one possible explanation for the correlation is that pyrite continues to increase with increasing organic carbon content because of the efficient accumulation of reactive iron. For example, calculations on the 35 samples in figure 8 that

have organic carbon contents between 3% and 12% show correlations, significant at the 95% confidence level, between organic carbon content and total iron (r = 0.48) and between organic carbon and reactive iron (that is, HCl-soluble iron plus pyritic iron [r = 0.66]). The ratio of reactive iron to total iron also increases with increasing organic carbon content of the samples. Also, under the strongly reducing conditions that produce organic matter-rich and finely laminated shales of lithofacies type IV, iron–sulfide reactions continue for a long time period, during which iron that is less reactive is perhaps also employed for pyrite formation.
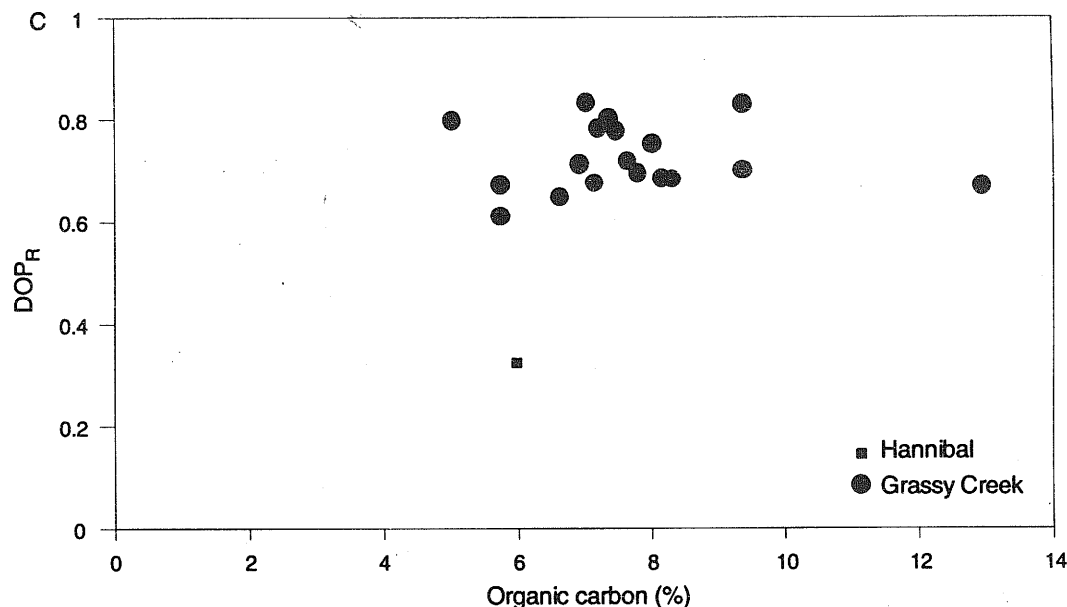
Figure 10   continued.

Samples with Anomalous Organic Carbon to Sulfur Ratios

Samples with low organic carbon to sulfur ratios
Random high-pyritic iron content is shown by 16 organic carbon-rich samples (fig. 4B). This group includes three samples with the lowest organic carbon to sulfur (C/S) ratios in a group of five high-pyrite samples from Wayne County core 13IL. These five samples of Grassy Creek Shale (S00412–S00416) have organic carbon concentrations between 6% and 9%, very high sulfur contents (>3.5%), very high iron concentrations (>4.5%), and consistently high DOP$_T$ values (>0.65). The sulfur and iron contents and DOP$_T$ values do not correlate with organic carbon content. The five samples are from successive 10-foot sections (5,090 to 5,140 ft) in the core; these thinly laminated shales show no evidence of bioturbation. The high pyrite contents in samples from one 50-foot section of the core suggest that euxinic conditions could have existed locally for a period of time during deposition of the Grassy Creek. Conversely, the sulfur isotope composition of pyrite in these samples does not show sufficient ^{34}S depletion to completely support the idea that euxinic conditions existed. Anderson et al. (1987) analyzed the pyrite in four of the samples (S00412–S00414, S00416) and found that $\delta^{34}S$ ranged from –17.6‰ to –4‰. These values are more positive than the values expected for euxinic conditions, that is, for conditions when sulfide forms in the water column and where access to ocean water sulfate is unlimited. For example, Beier and Hayes (1989) found $\delta^{34}S$ values of –40‰ to –30‰ for shale samples at the top of the Clegg Creek Member in Indiana, values that indicated to them syngenetic pyrite formed within an anoxic water column. Therefore, at least some of the pyrite in these samples from core 13IL formed within the sediments, and the sediments were at least partially closed to seawater sulfate.

The other 13 samples high in pyrite in figure 4B are (1) five samples from the cores 06IL, 02KY, 01KY, and 11IL, which were noted in table 2 and one sample (S00133 with Fe = 4.5% and S = 3.5%) in core 07IL; and (2) seven well cuttings samples that had significantly higher iron ($\geq \sim 2\sigma$ above the mean iron level for samples of their respective formations) and sulfur contents, including one Blocher Shale sample (S00241 with Fe = 5.3% and S = 5.3% on a carbonate-free basis).

These 13 samples are from widely scattered locations in the Illinois Basin and from various formations. Specific lithologic information is not available on the well cuttings samples. Lithologic characterization of the core samples (Bergstrom and Shimp 1978a, 1978b, 1979; Harvey, personal communication 1987) indicates all are from anoxic environments (lithofacies III or IV) that produced shale layers with even, parallel, and thin laminations, no bioturbation, and abundant small pyrite nodules distributed either randomly or along bedding planes. Thus, the high pyrite is not due to anomalous samples that contain large nodules. A high pyritic iron level could still occur, however, from sampling of shale with pyrite that is unevenly distributed along bedding planes. One explanation is that such erratic pyrite distribution in a sample reflects the local presence in later diagenetic stages of highly reducing and sulfide-rich conditions, which could result from inhomogeneous distribution of organic material or sulfate-reducing bacteria at the scale of microenvironments. If random high pyrite content does indicate a euxinic environment for any of these samples, then such an environment existed only within a narrow temporal or areal distribution.

Samples with high organic carbon to sulfur ratios
A group of 22 samples from 15 locations in the deep basin (fig. 2) that are characterized by higher than usual concentrations of trace metals (table 3) generally have

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Table 3 Summary of elemental concentrations in 22 metal-rich deep basin Grassy Creek samples and in metal-rich Hannibal Shale sample 07IL01L2 (S00127) compared with concentrations in all Grassy Creek and undifferentiated Grassy Creek/Sweetland Creek Shale samples.

	22 deep basin Grassy Creek		185 Grassy Creek and Grassy Creek/ Sweetland Creek[1]	
	Geometric mean	Range (s)	Geometric mean	Hannibal Shale Sample 07IL01L2
Organic C (%)	7.21	5.80–8.95	6.1	5.98
Total S (%)	1.58	1.16–2.14	2.3	0.44
Fe (%)	3.03	2.58–3.56	4.0	3.41
V (ppm)	426	324–560	210	1,600
Cr (ppm)	105	85–127	82	180
Co (ppm)	13	11–16	23	30
Ni (ppm)	115	86–152	84	260
Cu (ppm)	82	66–103	79	60
Zn (ppm)	403	218–744	150	1,100
As (ppm)	32	23–44	31	6.8
Se (ppm)	14	10–20	7 (38)[2]	12
Mo (ppm)	43	20–92	60	56
Ag (ppm)	0.9 (12)[2]	0.4–1.9	<0.2 (55)	<0.8
Sn (ppm)	6.7	5.3–8.6	6.6 (180)	17
Sb (ppm)	8.0	6.0–11	3.9	6.9
Pb (ppm)	37 (17)	18–37	37 (155)	42
U (ppm)	22	17–30	26	16

[1] From Frost et al. (1985, p. 23). Samples from core 11IL not included
[2] No. of samples with real values

high organic carbon to sulfur ratios. (The 22 samples are identified and the elemental concentrations are listed in Appendix 2.) All of these samples are from the top 30 feet of the Grassy Creek Shale in the deeper part of the Illinois Basin; however, the top of the Grassy Creek was not sampled from enough locations that it can be unequivocally stated that the layer with higher than usual trace metals concentrations is continuous (Frost et al. 1985, p. 69).

Results from the three cores (12IL, 13IL, and 01IN) indicate that the highest C/S ratios and the greatest enrichments in the metals are at the top of the Grassy Creek. With depth, the C/S ratios decrease and metal enrichments decline such that average values occur several feet down in the formation. Lithologic features (thinly laminated beds and little or no bioturbation) indicate the metal-rich core samples are from a completely anoxic environment.

Nineteen of the 22 samples plot in the high C/S field (fig. 4B), and the low level of pyrite is very noticeable in the samples with highest organic carbon contents. The samples have slightly lower iron contents than the average for the Grassy Creek Shale (table 3), and the iron contents are independent of the organic carbon contents (fig. 10A). The DOP_T values indicate an appreciable amount of nonpyritic iron in most of the samples (fig. 10B). However, DOP_R values determined for 18 samples show that little of this iron is reactive (fig. 10C); therefore, pyrite formation was probably iron-limited. The anomalously metal-rich sample

(S00127) of Hannibal Shale from core 07IL (noted in table 2 and included in table 3) has the same characteristics as the Grassy Creek samples, except that it has abundant reactive iron (fig. 10C).

Compared with average Grassy Creek Shale, the 22 samples contain twice as much vanadium and certain of the chalcophilic trace elements (Zn, Se, Sb, and Ag) and are slightly enriched in nickel and chromium. They generally contain the same amount of the chalcophilic elements Cu, As, Sn, and Pb as the average Grassy Creek Shale sample and lower amounts of cobalt and molybdenum than the average Grassy Creek Shale sample. Arsenic and cobalt are commonly concentrated in pyrite, so their low concentrations may be controlled by the low pyrite contents. Because the accumulated elements are chalcophilic, sphalerite (ZnS) and other trace metal sulfides (and perhaps antimonides and selenides) are likely to be present. Ripley et al. (1990) identified sphalerite, chalcopyrite, nickel-rich mackinawite, and clausthalite from electron microprobe analysis of shales from the New Albany in south-central and southeastern Indiana.

Lechler and Leininger (1978) also reported for the 01IN (Sullivan County) core higher concentrations of zinc, vanadium, and other trace metals in samples from the top of the Clegg Creek Member (equivalent to the upper part of the Grassy Creek in Indiana). Higher concentrations of zinc and the heavy metals V, Ag, Cd, Cr, Cu, Mo, Ni, and Pb were also found at the top of the Clegg Creek Member in cores from Marion, Brown,

and Clark Counties in south-central Indiana (Lechler et al. 1979). The greatest enrichment in trace metals found in shale of the New Albany in the Illinois Basin, however, was in these cores in the beds overlying the Clegg Creek. For example, in the top 1 to 2 inches of the organic carbon-rich Henryville Bed and in the thin, phosphatic Falling Run Bed (Lechler et al. 1979, Shaffer et al. 1981), vanadium concentrations were as high as 5,200 ppm and zinc concentrations were as high as 17,000 ppm. Ripley et al. (1990) also reported similarly high metal concentrations in the Henryville Bed in two cores from Bartholomew County, Indiana.

Hailer et al. (1982) described high ratios of carbon to sulfur, similar to values reported above, in the top 10 ft of the New Albany in cores from Sullivan, Marion, Brown, Jackson, and Clark Counties, Indiana (shown in fig. 2 and plotted in fig. 4B). Hasenmueller and Leininger (1987) state that the low-sulfur interval varies in thickness from 15.5 ft in northern Jackson County to 2.5 ft in Clark County.

Abundant evidence indicates that near the end of the deposition of the Grassy Creek Shale, the rate of sedimentation was very slow in the deep basin. Potter et al. (1980) found that in slowly deposited sediments there is a greater accumulation of vanadium relative to nickel, presumably because organic matter long in contact with seawater absorbs more vanadium. Hence, the fact that the 22 deep basin samples are much more enriched in vanadium than in nickel suggests slow sedimentation. Hailer et al. (1982) related the low ^{34}S content of the pyritic sulfur in the Henryville and other beds at the top of the New Albany, in Brown, Clark, Harrison, Jackson, Marion, and Sullivan Counties, to a slow rate of clastic sedimentation at the close of the deposition of the New Albany. From lithologic characteristics of marker beds in several cores and stratigraphic relations between them, Lineback (1969) concluded that by the end of the Devonian or the beginning of the Mississippian, sediment-starved basin conditions prevailed in the deeper part of the Illinois Basin.

Sedimentation probably slowed as the sea in the Illinois Basin deepened (due to basin subsidence) at the end of the deposition of the Grassy Creek Shale. Because the water column was stratified and there was little circulation or oxygenation of the colder, denser bottom waters, organic matter-rich shales were preserved in the anaerobic conditions at the bottom of the sea. The sea probably continued to deepen as the Hannibal Shale was being deposited in southeastern Illinois. Eastward in Indiana, little sediment was deposited. Ettensohn and Barron (1982) suggest that the

sea depth eventually increased to the point that upwelling oceanic waters off the continental margin to the south spilled over into the epicontinental Devonian Sea; greater amounts of phosphate and heavy metals (in the Falling Run and Henryville Beds), as well as much organic matter, accumulated in sediments settling from these nutrient-rich waters. Beier and Hayes (1989) consider a bloom in the production of organic matter as a principal cause for the phenomenom of the Falling Run and Henryville Beds.

Blocher Shale Formation

The relationships between carbon, sulfur, and iron in the New Albany Group formations discussed in previous sections do not apply to the calcareous and dolomitic Blocher Shale. Twenty-four samples of Blocher Shale were analyzed; they had CO_2 contents equivalent to 7.4% to 46.8% dolomite plus calcite. These calculations assume that all calcium is present in carbonate and that the remainder of the carbonate carbon is balanced by magnesium.

Results summarized for the Blocher Shale, both on the whole sample and carbonate-free sample basis (table 2), show that sulfur content bears no relationship to organic carbon content. Low iron and relatively high and constant DOP_T values indicate iron-limited pyrite formation.

Iron correlates with the detrital content, as estimated by clay and quartz, in the set of samples (the correlation coefficient between iron and aluminum is 0.62, significant at the 95% confidence level). The iron limitation arises, as expected, because iron-rich clays are diluted with iron-poor carbonate. For the five Blocher samples analyzed for HCl-soluble iron, high DOP_R values of 0.73 to 0.96 (fig. 8) suggest iron-limited pyrite formation.

Pyrite would be expected to be iron-limited in nearly pure carbonate samples. Gibson (1985), who studied organic-rich calcareous siltstones of the Cambrian Currant Bush Limestone in Australia, reported that iron was a major limiting factor in pyrite formation in rocks with carbonate as low as 32%.

Organic carbon concentrations in the 24 samples of Blocher Shale analyzed ranged from 3.3% to 9.0% (5.2% to 12.1% on the carbonate-free basis). The consistent organic richness of the Blocher Shale and the high DOP values support the interpretation offered by Cluff (1980) that the Blocher was deposited in an anoxic deep-water environment; but the carbon, sulfur, and iron relationships do not further define the depositional environment.

SUMMARY AND CONCLUSIONS

In 374 samples from the New Albany Group in the Illinois Basin, mainly from within Illinois, the concentration of total sulfur, which is taken as a reliable measure of pyritic sulfur, generally correlates with organic carbon content. The relationship is consistent with the

theory that bacterial reduction of sulfate concomitant with bacterial oxidation of organic matter in the sediments controls sulfide production and pyrite formation. An increase in the production and deposition of organic matter leads, particularly in deep water with

restricted circulation, to increasingly anoxic conditions. Such conditions favor the growth and functioning of anaerobic, sulfate-reducing bacteria, which, in turn, govern the formation of sulfide.

Conditions for preservation of organic material in shale varied widely in the Devonian–Mississippian sea in the Illinois Basin. Lithofacies data from Harvey et al. (1977), Cluff (1980), and Cluff et al. (1980) confirm that progressively greater amounts of organic carbon preserved in the shale correlate with progressively anaerobic conditions. Such conditions were probably controlled by paleogeography, and correlate with the regional setting of the New Albany Shales proposed by Cluff (1980).

The greenish gray Saverton and Hannibal Shales were sampled mainly from the northwest part of the Illinois Basin. These samples have organic carbon contents generally ranging from 0.2% to 2% and organic carbon to sulfur ratios averaging about 1.8 and reflect a depositional environment that was generally shallow and primarily dysaerobic. The degree of pyritization of iron (total or reactive) increases rapidly with organic carbon content; this increase is an expected consequence of the high ratio of sulfur to carbon.

The Sweetland Creek Shale and part of the Grassy Creek Shale in western Illinois also are relatively low (1% to 3%) in organic carbon content. Organic carbon content in those units generally increases southeastward across the shelf margin, basin slope, and into the deep basin (Frost 1980, fig. X-2). The brownish black and black shales of the Grassy Creek and Blocher Formations in southeastern Illinois have organic carbon contents generally of 4% to 9% and as high as 15%. Increasing carbon content indicates increasingly anoxic depositional environments. In these samples, sulfur correlates with organic carbon content, and the average ratio of organic carbon to sulfur is 2.8. DOP_T and DOP_R also generally correlate with organic carbon content. Variability in the iron content of the samples produces a great deal of scatter in the plots of DOP against organic carbon, especially as organic carbon content increases to a level at which average iron content becomes the limiting factor to pyrite formation.

Pyrite formation was found to be iron-limited in the Blocher Shale, which contains abundant carbonate.

Iron levels in the shales were generally related to the clastic or detrital content. A small increase in total iron content as carbon content increases is probably due to adsorption or complexation between iron compounds and organic material. A small increase in the reactive iron content as organic carbon content increases provides sufficient iron for pyrite content to increase and correlate with organic carbon content that is as high as 15%.

This study, because it was able to draw on information for a very large number of samples, contributes to a comphrehensive picture of the paleoenvironments that existed during deposition of the New Albany Group in the Illinois part of the Illinois Basin. But the picture is not complete, particularly with respect to explaining the changes in conditions that led to changes in formations in different parts of the Illinois Basin.

No evidence from this study substantiates the existence of widespread euxinic conditions in the Illinois Basin within Illinois during the deposition of the New Albany Group. Completely anoxic conditions no doubt prevailed in the deep basin in southeastern Illinois during deposition of finely laminated shales, particularly of the Blocher and Grassy Creek Shales. Under these conditions, some hydrogen sulfide probably diffused out of those sediments into the seawater.

In contrast, Beier and Hayes (1989) and Ripley et al. (1990) concluded that formation of iron sulfide in a hydrogen sulfide-bearing water column was significant during the deposition of the upper part of the Clegg Creek Member and in the overlying Falling Run and Henryville Beds in southern Indiana, where deposition was on a deep shelf (fig. 2). The same deep shelf conditions appear consistent with the data (table 2) for the Bullitt County, Kentucky, core (02KY). Interpretation of the depositional environment for this core was not addressed in this report because it is regionally isolated with respect to the rest of the data points. More data are needed from southwestern Indiana and northwestern Kentucky to document differences in conditions between the deep basins in those areas and in southeastern Illinois and the eastern and southern margins of the Basin during Devonian and Mississippian time.

REFERENCES

Anderson, T.F., J. Kruger, and R. Raiswell, 1987, C–S–Fe relationships and the isotopic composition of pyrite in the New Albany Shale of the Illinois Basin, U.S.A.: Geochimica et Cosmochimica Acta v. 51, p. 2795–2805.

Barrows, M.H., R.M. Cluff, and R.D. Harvey, 1980, Organic petrography, *in* R.E. Bergstrom, N.F. Shimp, and R.M. Cluff, Geologic and Geochemical Studies of the New Albany Shale Group (Devonian–Mississippian) in Illinois: Final Report by the Illinois State Geological Survey to the U.S. Department of Energy under Contract DE-AC21-76ET12142, Chapter VIII, p. 63–75.

Beier, J.A., and J.M. Hayes, 1989, Geochemical and isotopic evidence for paleoredox conditions during deposition of the Devonian–Mississippian New Albany Shale, southern Indiana: Geological Society of America Bulletin, v. 101, p. 774–782.

Bergstrom, R.E., and N.F. Shimp, 1978a, Geologic and geochemical studies of the New Albany Group (Devonian black shale) in Illinois to evaluate its characteristics as a source of hydrocarbons: Quarterly

Progress Report for July 1–September 30, 1978, by the Illinois State Geological Survey to the U.S. Department of Energy under Contract EY-76-C-05-5203. Report No. ORO-EY-76-C-05-5203-12, p. 28–32.

Bergstrom, R.E., and N.F. Shimp, 1978b, Geologic and geochemical studies of the New Albany Group (Devonian black shale) in Illinois to evaluate its characteristics as a source of hydrocarbons: Quarterly Progress Report for October 1–December 31, 1978, by the Illinois State Geological Survey to the U.S. Department of Energy under Contract EY-76-C-05-5203. Report No. ORO-EY-76-C-05-5203-3, p. 8–12.

Bergstrom, R.E., and N.F. Shimp, 1979, Geologic and geochemical studies of the New Albany Group (Devonian black shale) in Illinois to evaluate its characteristics as a source of hydrocarbons: Monthly Progress Report for May 1979, by the Illinois State Geological Survey to the U.S. Department of Energy under Contract DE-AC21-76-MC05203. Report No. ORO-DE-AC21-76-MC05203-8, 30 p.

Bergstrom, R.E., N.F. Shimp, and R.M. Cluff, 1980, Geologic and geochemical studies of the New Albany Shale Group (Devonian–Mississippian) in Illinois: Final Report by the Illinois State Geological Survey to the U.S. Department of Energy under Contract DE-AC21-76ET12142, 183 p.

Berner, R.A., 1970, Sedimentary pyrite formation: American Journal of Science, v. 268, p. 1–23.

Berner, R.A., 1984, Sedimentary pyrite formation—An update: Geochimica et Cosmochimica Acta, v. 48, p. 605–615.

Boesen, C., and D. Postma, 1988, Pyrite formation in anoxic environments of the Baltic: American Journal of Science, v. 288, p. 575–603.

Byers, C.W., 1977, Biofacies patterns in euxinic basins—A general model, in Deep-water Carbonate Environments, H.E. Cook and P. Enos, editors: Society of Economic Paleontologists and Mineralogists Special Publication no. 25, p. 5–17.

Cluff, R.M., 1980, Paleoenvironment of the New Albany Shale Group (Devonian–Mississippian) of Illinois: Journal of Sedimentary Petrology, v. 50, p. 767–780.

Cluff, R.M., R.D. Harvey, D.A. Burke, and M.H. Barrows, 1980, Petrography and depositional environment, in R.E. Bergstrom, N.F. Shimp, and R.M. Cluff, Geologic and Geochemical Studies of the New Albany Shale Group (Devonian–Mississippian) in Illinois: Final Report by the Illinois State Geological Survey to the U.S. Department of Energy under Contract DE-AC21-76ET12142, Chapter VI, p. 39–49.

Cluff, R.M., M.L. Reinbold, and J.A. Lineback, 1981, The New Albany Shale Group of Illinois: Illinois State Geological Survey Circular 518, 83 p.

Devera, J.A., and N.R. Hasenmueller, 1991, Kaskaskia Sequence: Middle and Upper Devonian Series through Mississippian Kinderhookian Series, in Interior Cratonic Basins, M.W. Leighton, D.R. Kolata, D.F. Oltz, and J.J. Eidel, editors: American Association of Petroleum Geologists Memoir 51, Chapter 8, p. 113-123.

Dickerson, D.R., 1980, Mode of occurrence and relative distribution of hydrocarbon phases in shale, in R.E. Bergstrom and N.F. Shimp, Geologic and Geochemical Studies of the New Albany Group (Devonian Black Shale) in Illinois to Evaluate its Characteristics as a Source of Hydrocarbons: Quarterly Progress Report for October 1–December 31, 1979, by the Illinois State Geological Survey to the U.S. Department of Energy under Contract DE-AC21-76-MC05203. Report ORO-DE-AC21-76-MC05203-3, p. 9–12, 26–34.

Dickerson, D.R., and M.-I.M. Chou, 1980, Hydrocarbon content and composition, in R.E. Bergstrom, N.F. Shimp, and R.M. Cluff, Geologic and Geochemical Studies of the New Albany Shale Group (Devonian–Mississippian) in Illinois: Final Report by the Illinois State Geological Survey to the U.S. Department of Energy under Contract DE-AC21-76ET12142, Chapter XII, p. 115–134.

Donnelly, T.H., J.H. Shergold, and P.N. Southgate, 1988, Pyrite and organic matter in normal marine sediments of Middle Cambrian age, southern Georgina Basin, Australia: Geochimica et Cosmochimica Acta, v. 52, p. 259–263.

Ettensohn, F.R., and L.S. Barron, 1982, A tectonic-climatic approach to the deposition of the Devonian–Mississippian black-shale sequence of North America: Proceedings of the 1982 Eastern Oil Shale Symposium, Kentucky Department of Energy and the University of Kentucky Institute for Mining and Minerals Research, Lexington, KY, Oct. 11–13, 1982, p. 5–37.

Fisher, I. St. J., 1986, Pyrite formation in bioturbated clays from the Jurassic of Britain: Geochimica et Cosmochimica Acta, v. 50, p. 517–523.

Frost, J.K., 1980, Chemical analysis of Devonian shales—Organic carbon content, in R.E. Bergstrom, N.F. Shimp, and R.M. Cluff, 1980, Geologic and Geochemical Studies of the New Albany Shale Group (Devonian–Mississippian) in Illinois: Final Report by the Illinois State Geological Survey to the U.S. Department of Energy under Contract DE-AC21-76ET12142, p. 95–105.

Frost, J.K., D.L. Zierath, and N.F. Shimp, 1985, Chemical composition and geochemistry of the New Albany Shale Group (Devonian–Mississippian) in Illinois: Illinois State Geological Survey Contract Report 1985-4, 134 p. *Note: Errors corrected in the compilation of chemical data in Frost et al. (1985) are: for S00301 (NAS-0402), S = 0.99% (decimal point error); for S00429 (13IL26C3) and S00430 (13IL27C1), SiO_2 = 42.64% and 44.06%, Al_2O_3 = 7.64% and 8.43%, FeO = 1.95% and 2.57%, MgO = 3.54% and 4.07%, CaO = 17.77% and 16.11%, TiO_2 = 0.33% and 0.38%, P_2O_5 = 0.07%, and 0.08%, respectively (analyst had reversed the two samples).

Gibson, D.L., 1985, Pyrite–organic matter relationships—Currant Bush Limestone, Georgina Basin,

Australia: Geochimica et Cosmochimica Acta, v. 49, p. 989–992.

Goldhaber, M.B., and I.R. Kaplan, 1974, The sulfur cycle, in The Sea, v. 5, E.D. Goldberg, editor, John Wiley and Sons, New York, p. 569–655.

Hailer, J.G., N.R. Shaffer, R.K. Leininger, E.M. Ripley, and M.G. Yates, 1982, Sulfur and carbon isotope trends in the New Albany Shale (Devonian and Mississippian) in Indiana: Proceedings of the 1982 Eastern Oil Shale Symposium, Kentucky Department of Energy and the University of Kentucky Institute for Mining and Minerals Research, Lexington, KY, Oct. 11–13, 1982, p. 127–135.

Harvey, R.D., D.A. Burke, M.H. Barrows, and R.M. Cluff, 1980, Mineralogy, in R.E. Bergstrom, N.F. Shimp, and R.M. Cluff, Geologic and Geochemical Studies of the New Albany Shale Group (Devonian–Mississippian) in Illinois: Final Report by the Illinois State Geological Survey to the U.S. Department of Energy under Contract DE-AC21-76ET12142, Chapter VII, p. 51–61.

Harvey, R.D., W.A. White, R.M. Cluff, J.K. Frost, and P.B. DuMontelle, 1977, Petrology of the New Albany Shale Group (Upper Devonian and Kinderhookian) in the Illinois Basin—A preliminary report: Proceedings of the First Eastern Gas Shales Symposium, Morgantown, WV, Oct. 17–19, 1977. MERC/SP-77/5, p. 239–265.

Hasenmueller, N.R., and R.K. Leininger, 1987, Oil–shale prospects for the New Albany Shale in Indiana: Indiana Geological Survey Special Report 40, 31 p.

Hasenmueller, N.R., and G.S. Woodard, editors, 1981, Studies of the New Albany Shale (Devonian and Mississippian) and equivalent strata in Indiana: Contract Report by the Indiana Geological Survey, Bloomington, to the U.S. Department of Energy, Morgantown, WV, under Contract No. DE-21-76MC05204, 100 p.

Hirst, D.M., 1974, Geochemistry of sediments from eleven Black Sea cores, in The Black Sea—Geology, Chemistry and Biology, E.T. Degens and D.A. Ross, editors, American Association of Petroleum Geologists Memoir 20, p. 430–455.

Lechler, P., and R.K. Leininger, 1978, Analysis of black shale by inductively coupled plasma: Preprints, Second Eastern Gas Shales Symposium, Morgantown Energy Technology Center, Morgantown, WV, METC/SP-78/6, v. 1, p. 273–279.

Lechler, P.J., N.R. Hasenmueller, J.L. Bassett, and R.K. Leininger, 1979, Distribution and geochemical characterization of the Hannibal Member of the New Albany Shale in Indiana: Proceedings, Third Eastern Gas Shales Symposium, Oct. 1–3, 1979, Morgantown Energy Technology Center, Morgantown, WV, METC/SP-79/6, p. 511–525.

Leventhal, J.S., 1983, An interpretation of carbon and sulfur relationships in Black Sea sediments as indicators of environments of deposition: Geochimica et Cosmochimica Acta, v. 47, p. 133–137.

Leventhal, J.S., 1987, Carbon and sulfur relationships in Devonian shales from the Appalachian Basin as an indicator of environment of deposition: American Journal of Science, v. 287, p. 33–49.

Lineback, J.A., 1969, Illinois Basin—Sediment-starved during Mississippian: American Association of Petroleum Geologists Bulletin, v. 53, p. 112–126.

Lineback, J.A., 1980, Coordinated study of the Devonian black shale in the Illinois Basin—Illinois, Indiana, and western Kentucky: Final Report by the Illinois State Geological Survey to the U.S. Department of Energy, Morgantown Energy Technology Center, Morgantown, WV, under Contract DE-AS21-78MC08214. Illinois State Geological Survey Contract Report 1981-1, 36 p.

Middelburg, J.J., 1991, Organic carbon, sulphur, and iron in semi-euxinic sediments of Kau Bay, Indonesia: Geochimica et Cosmochimica Acta, v. 55, p. 815–828.

Nelson, W.J., 1995, Bedrock Geology of the Paducah 1° x 2° Quadrangle, Illinois, Kentucky, and Missouri: Illinois State Geological Survey Bulletin 102, 40 p.

Potter, P.E., J.B. Maynard, and W.A. Pryor, 1980, Special geological, geochemical and petrological studies of the Devonian shales in the Appalachian Basin: Final Report from the Department of Geology, University of Cincinnati to the U.S. Department of Energy Eastern Gas Shales Project, Contract DE-AC21-76MC05201, 86 p.

Raiswell, R., and R.A. Berner, 1985, Pyrite formation in euxinic and semi-euxinic sediments: American Journal of Science, v. 285, p. 710–724.

Rhoads, D.C., and J.W. Morse, 1971, Evolutionary and ecologic significance of oxygen-deficient marine basins: Lethaia v. 4, p. 413–428.

Ripley, E.M., N.R. Shaffer, and M.S. Gilstrap, 1990, Distribution and geochemical characteristics of metal enrichment in the New Albany Shale (Devonian–Mississippian), Indiana: Economic Geology, v. 85, p. 1790–1807.

Shaffer, N.R., R.K. Leininger, E.M. Ripley, and M.S. Gilstrap, 1981, Heavy metals in organic-rich New Albany Shale of Indiana: Abstracts with Programs, Annual Meeting of the Geological Society of America, Cincinnati, Nov. 2–5, 1981, v. 13, no. 7, p. 551 (abstr.).

Sweeney, R.E., 1972, Pyritization during diagenesis of marine sediments: Ph.D. thesis, University of California, Los Angeles, 200 p.

Appendix 1 Concentrations of total iron and HCl-soluble iron in 71 samples from the New Albany Group determined by atomic absorption spectrophotometry, and DOP$_R$ calculated from pyritic iron and HCl-soluble iron concentrations. Samples are described in Frost et al. (1985).

Geol. no.	Sample no.	Total Fe* as FeO (%)	HCl-soluble Fe as FeO (%)	DOP$_R$
06IL05C1	S00074	4.78	2.34	0.079
06IL07C1	S00076	3.88	2.01	0.18
06IL09C1	S00078	4.81	2.46	0.12
06IL11C1	S00080	5.27	2.09	0.27
06IL13C1	S00082	4.93	1.90	0.27
06IL15C1	S00084	5.10	1.77	0.36
06IL17C1	S00086	5.00	1.48	0.56
06IL19C1	S00088	5.45	1.17	0.66
06IL21C1	S00090	5.64	1.40	0.64
06IL22C1	S00091	4.78	0.944	0.65
06IL23C1	S00092	5.28	1.73	0.55
06IL24C1	S00093	3.39	1.22	0.50
06IL25C1	S00094	4.04	0.815	0.71
07IL01L2	S00127	4.07	1.03	0.32
11IL02C1	S00330	3.71	0.442	0.88
11IL04C1	S00332	4.08	2.13	0.52
11IL14C1	S00342	4.36	2.40	0.46
11IL15C1	S00343	3.78	1.53	0.57
11IL16C1	S00344	3.44	1.82	0.49
12IL01C1	S00402	5.78	0.706	0.83
12IL01C2	S00403	4.28	0.814	0.68
12IL01C3	S00404	3.35	0.525	0.69
12IL01C4	S00405	4.41	0.600	0.79
13IL04C1	S00407	3.60	1.75	0.34
13IL05C1	S00408	3.79	0.652	0.64
13IL07C2	S00410	3.46	0.902	0.67
13IL08C1	S00411	2.72	0.302	0.83
13IL10C1	S00413	5.61	0.626	0.87
13IL12C3	S00415	6.45	0.582	0.89
13IL14C3	S00417	5.24	1.02	0.75
13IL16C2	S00419	5.17	0.988	0.74
13IL18C2	S00421	5.14	1.36	0.65
13IL19C1	S00422	4.42	1.82	0.46
13IL21C2	S00424	3.92	1.02	0.61
13IL23C4	S00426	4.68	0.721	0.80
13IL26C3	S00429	1.74	0.058	0.96
13IL27C1	S00430	2.23	0.077	0.96
01IN01C1	S00352	3.64	0.728	0.67
01IN01C2	S00353	3.50	0.760	0.70
01IN02C1	S00354	4.10	0.836	0.71
01IN11C1	S00372	5.53	1.22	0.74
01KY07C1	S00007	6.03	1.11	0.81
01KY08L1	S00033	4.59	1.96	0.58
NAS-0061	S00152	4.86	1.22	0.61
NAS-0065	S00154	3.88	0.739	0.71
NAS-0093	S00180	3.38	0.511	0.80
NAS-0095	S00182	4.69	0.995	0.69
NAS-0114	S00191	4.48	1.05	0.78
NAS-0119	S00195	4.33	0.604	0.84
NAS-0123	S00198	4.67	1.28	0.62
NAS-0126	S00201	2.80	0.772	0.73
NAS-0129	S00202	3.50	0.866	0.68
NAS-0131	S00204	3.39	0.464	0.85
NAS-0159	S00215	4.04	0.593	0.72
NAS-0166	S00219	4.17	0.779	0.68
NAS-0185	S00227	5.18	0.955	0.70
NAS-0189	S00228	5.31	0.773	0.82
NAS-0208	S00237	4.85	1.68	0.58
NAS-0213	S00239	3.31	0.552	0.75
NAS-0247	S00254	4.99	0.579	0.85
NAS-0249	S00255	3.36	0.484	0.84
NAS-0253	S00257	3.79	0.716	0.74
NAS-0320	S00277	5.58	1.61	0.66
NAS-0343	S00283	4.14	0.771	0.76
NAS-0360	S00289	5.09	1.80	0.58
NAS-0396	S00299	4.06	1.16	0.64
NAS-0421	S00306	4.72	0.949	0.77
NAS-0427	S00308	3.04	0.524	0.77
NAS-0431	S00309	6.06	3.08	0.42
NAS-0447	S00313	4.23	1.01	0.67
NAS-0451	S00314	4.23	1.50	0.55

*Procedure Replicate 0.1 g samples of dried 500°C ash (used because organic matter in the whole shale interferes in a wet acid digestion) were digested in hydrofluoric acid and aqua regia. Excess hydrofluoric acid was complexed with boric acid, and the solution was taken to 50 mL volume with water for measurement of iron. Average mean error between replicates was 0.7% relative.

Appendix 2 Elemental concentrations in 22 samples of Grassy Creek Shale from the deep basin area of the Illinois Basin characterized by unusually high levels of some trace metals.

Sample no.	Geologic no.	Organic C (%)	Total S (%)	Fe (%)	V (ppm)	Cr (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	As (ppm)	Se (ppm)	Mo (ppm)	Ag (ppm)	Sn (ppm)	Sb (ppm)	Pb (ppm)	U (ppm)
S00150	NAS-0057	6.97	1.55	2.95	650	110	11	110	95	540	25	16	45	<0.7	8.3	9.4	58	22
S00152	NAS-0061	5.74	1.69	3.55	430	93	17	95	72	370	30	11	52	<0.8	6.0	6.5	65	23
S00154	NAS-0065	6.93	1.62	2.87	530	100	12	110	91	550	33	15	53	<0.8	7.5	7.6	46	21
S00157	NAS-0070	5.21	0.96	2.94	600	110	13	100	65	300	23	13	22	<0.8	8.3	5.9	36	15
S00180	NAS-0093	7.37	1.82	2.39	65	76	11	130	69	330	40	9.8	110	<2.0	5.4	9.7	*	33
S00191	NAS-0114	7.21	3.31	3.50	570	110	17	130	86	450	40	24	47	<2.0	6.6	11	*	26
S00202	NAS-0129	8.16	1.66	2.57	390	78	12	130	60	380	30	8.0	140	<2.0	6.4	7.0	*	37
S00215	NAS-0159	7.65	1.34	2.99	530	110	15	130	76	550	36	14	79	<2.0	9.3	8.0	*	23
S00219	NAS-0166	8.32	1.49	3.19	440	110	11	86	66	340	21	14	31	<2.0	7.4	6.4	*	17
S00236	NAS-0207	6.89	2.18	3.29	340	82	15	71	51	370	37	8.0	77	<1.9	5.3	7.2	93	27
S00239	NAS-0213	8.03	1.47	2.64	380	120	11	140	89	560	28	18	51	1.5	6.5	9.4	33	21
S00308	NAS-0427	7.48	1.62	2.49	330	81	12	130	68	520	28	12	89	1.2	6.8	9.1	22	29
S00352	01IN01C1	12.96	1.30	3.23	520	150	26	290	130	3,600	41	25	89	3.7	5.4	12	96	32
S00353	01IN01C2	9.38	1.57	2.98	430	110	11	120	99	510	35	22	40	1.4	<4.1	11	55	20
S00402	12IL01C1	9.38	3.01	4.72	450	140	14	140	110	290	92	22	51	1.8	5.9	14	120	24
S00403	12IL01C2	5.74	1.52	3.57	280	120	14	110	110	280	25	13	22	0.36	11	4.8	41	15
S00404	12IL01C3	7.80	1.05	2.71	430	120	12	120	97	380	21	16	26	1.1	6.7	7.6	22	17
S00405	12IL01C4	5.03	2.07	3.59	270	110	12	100	80	150	31	17	9	0.56	4.8	8.4	21	15
S00408	13IL05C1	6.63	1.06	3.25	260	140	16	110	73	240	42	15	7	0.43	8.8	4.8	51	10
S00409	13IL06C2	5.31	1.17	2.80	310	100	12	70	99	180	32	12	23	0.45	6.9	5.7	16	17
S00410	13IL07C2	7.15	1.66	2.99	440	87	11	94	86	560	18	12	67	1.1	9.3	7.3	8.6	22
S00411	13IL08C1	7.04	1.31	2.37	470	91	13	120	85	270	30	10	65	0.46	5.9	9.0	16	32

* Lead was not accurately determined

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