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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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ENTITLED SULFUR ISOTOPES IN THE DEVONIAN

NEW ALBANY SHALE

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF BACHELOR OF SCIENCE IN GEOLOGY

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SULFUR ISOTOPES IN THE DEVONIAN NEW ALBANY SHALE

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THESIS

for the

DEGREE OF BACHELOR OF SCIENCE

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Sulfur isotopic analyses were performed on New Albany Shale (Late Devonian) samples from the two cores in the Illinois Basin. The purpose of the study was to evaluate the extent of isotopic fractionation in the reduction of sulfate to sulfide during early diagenesis of organic rich sediments and to examine factors which controlled the extent of fractionation. $\delta^{34}S$ values generally decrease from the base of the shale to the top. Fractionation between pyrite and sea water sulfate ($\Delta^{34}S$) was calculated using the sulfate-age curve of Claypool et al. (1980). $\Delta^{34}S$ values appear to be inversely related to the estimated isotopic composition of contemporaneous sea-water sulfate. Neither $\delta^{34}S$ nor $\Delta^{34}S$ values show a clear relationship to inferred sedimentation rates. $\delta^{34}S$ values show an inverse relationship to organic carbon content, but $\Delta^{34}S$ values do not. The results suggest that factors which controlled isotopic fractionation during bacterial sulfate reduction in the New Albany Shale were different from those which control fractionation in modern marine sediments.
I would like to thank Professor T. F. Anderson for his patient guidance in supervising this study and preparing the thesis. Linda Westgate and Keith Hackley were of invaluable aid in helping with extraction procedures. Keith also gave service beyond the call of duty by discussing ideas, sharing references, and keeping the mass spectrometer (MAT) in operation. Mary Barrows of the Illinois State Geological Survey helped cut red tape in procuring samples, and it is appreciated. Thanks also to Dennis Coleman of the USGS. Special thanks to Professor R. L. Langenheim, Jr. for his patient, caring, concerned, courteous, dedicated, unselfish, interested, and eager help in deciphering the stratigraphy. Pius Weibel helped there too. Carol Sanderson did the typing.
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CHAPTER 1
INTRODUCTION

Long-term control of sulfur and carbon cycles and hence of molecular oxygen flux to and from the atmosphere is currently the subject of controversy (Garrels and Lerman, 1981; Anderson et al., 1982; Berner and Raiswell, in press). Models have been proposed which suggest that rapid deposition and preservation of the reduced form of one element must be accompanied by deposition of the oxidised form of the other in order to maintain a relatively constant supply of oxygen in the atmosphere (Garrels and Lerman, 1982). Isotope information from the rock record may aid in understanding the relationship between sulfur and carbon. Isotopes of both elements are fractionated during certain biological processes. When sulfate ion is reduced by anaerobic bacteria, $^{32}\text{S}$ is concentrated in the reduced form. Similarly, reduced carbon in organic matter is enriched in $^{12}\text{C}$. By measuring changes in $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ as preserved in carbonates and sulfate minerals, it should be possible to check these models and estimate mass fluxes of reduced and oxidised C and S through time.

It is known that the isotopic composition of sulfate in sea water has changed through time and undergone periods of rapid change (Claypool et al., 1980), probably in response to mass fluxes of reduced and oxidised S. One such event, a sudden shift to more positive $\delta^{34}\text{S}$ values occurred in the Late Devonian. The probable cause for this shift is uptake of isotopically light sulfur into pyrite in black shales, since the pyrite in these shales is primarily formed from reduction of light $\text{H}_2\text{S}$ liberated by anaerobic bacterial sea water sulfate reduction. Some record of this event should exist in pyritic, organic rich black shales; such as the New Albany Shale (Late Devonian) of the
Illinois Basin. The nature and extent of the recorded sulfate isotope change in such shales, however, is uncertain.

The purpose of this paper is to evaluate the extent of isotopic fractionation in the reduction of sulfate to sulfide during the early diagenesis of organic rich sediments and to examine the factors which controlled the extent of fractionation. In order to study this, twenty samples of New Albany Shale, recovered as core from the Illinois Basin were analysed for pyrite sulfur isotopic composition. These wells were located in Southern Wayne Co., Illinois and Western Sullivan Co., Indiana (see Fig. 1 and Appendix).
Figure 1. Location map of sample sites.
(● = well location)
(From Cluff et al., 1981)
CHAPTER 2

GEOLOGY OF THE NEW ALBANY SHALE

Stratigraphy

The New Albany Shale is part of the Knobs Megagroup in Illinois (Collinson and Atherson, 1975). It consists predominantly of green, gray, and black Middle Devonian to Lower Mississippian shales (Collinson and Atherson, 1975; Cluff et al., 1981) and is found in the Illinois, Indiana, and Kentucky portions of the Illinois Basin. The group has a maximum thickness of 460 feet in southeastern Illinois and western Kentucky (Fig. 2). Throughout most of the Illinois Basin it overlies the Huntington Limestone Megagroup (Middle Devonian). In the central part of the basin it is overlain by the Chouteau Limestone (Cluff et al., 1981).

The Illinois State Geological Survey divides the New Albany Shale Group into nine formations (Cluff et al., 1981). The current divisions of the group contain some modifications of formation boundaries and lithologies, and the nomenclature used for this report is the same as defined by Cluff et al. (1981).

The formations of the New Albany Shale Group from oldest to youngest are:

1. Blocher Shale
2. Sylamore Shale
3. Selmaier Shale
4. Sweetland Creek Shale
5. Grassy Creek Shale
6. Saverton Shale
7. Louisiana Limestone
8. Horton Creek Formation
9. Hannibal Shale

These formations do not occur as a complete stratigraphic sequence at any one locality and each formation grades laterally into one or more of the others (Cluff et al., 1981).
Figure 2. Thickness map of New Albany Shale Group.
For this study, samples from the Blocher, Selmier, Grassy Creek, and Hannibal Shales were analyzed. These formations form an uninterrupted stratigraphic sequence in eastern Illinois and western Indiana. The following descriptions of these units are from Cluff et al. (1981):

**Blocher Shale:** The calcareous black shale at the base of the New Albany Group. It consists of laminated brownish and grayish black shales. The Blocher is calcareous, carbonaceous, and contains small nodules and lenses of pyrite which are often concentrated along bedding planes. Fossils are relatively common and are planktonic, nektic, or show signs of transport. This is a slightly more restricted definition of the shale than as originally defined by Borden (1874). Conodont evidence indicates that nearly all the unit is Middle Devonian (Givetian) in age (see Fig. 3).

**Selmier Shale:** The alternating greenish gray, gray, and black shales which underlie the dominantly black Grassy Creek Shale and overlie the calcareous black shale of the Blocher. The dark shales have thick, discontinuous, widely spaced lamellae. Pyrite nodules are common. Indistinctly bedded shales are extensively, but not totally, burrowed. Conodonts of the upper Selmier Shale show correlation with European goniatite zones to I and perhaps to II (Frasnian to Early Famennian) (see Fig. 4).

**Grassy Creek Shale:** The dominantly black shale interval of the middle and upper part of the New Albany Shale Group. The Grassy Creek grades from olive gray to olive black carbonaceous shales with thin beds of mudstone in the north to grayish black and brownish black finely laminated pyritic carbonaceous shales in southern Illinois and western Kentucky. Pyrite occurs as small nodules and lenses, scattered large nodules, and scattered framboids. In Wayne Co. the top of the Grassy Creek is Uppermost Devonian. Cluff et al. (1981) state that where the greenish gray shales assignable to the Hannibal-Saverton are absent, the uppermost black shale of the Grassy Creek is probably Tournaisian (Lowest Mississippian) in age. This is the case at the Sullivan Co. location (Fig. 3).

---

**Depositional Environment and Paleogeography**

Most of the New Albany Shale Group was apparently deposited in a deep (>150 m) anoxic basin. Rock type distributions indicate that the basin was
Figure 3. **Thickness map of Blocher Shale.**

- @= well location.
- (From Cluff et al., 1981.)
Figure 4. Thickness map of Selkirk Shale.
- well location
(From Cleff et al., 1981.)
Figure 5a. Thickness map of Grassy Creek Shale.

G = well location
(From Cluff et al., 1981).
Figure 5b. Thickness map of Hannibal Shale.
- Map location.

(From Cluff et al., 1981)
stratified with respect to oxygen and centered in southeastern Illinois and western Kentucky (Fig. 2) (Cluff et al., 1981). This conclusion was based on occurrence of fossils and bioturbation, thickness, and distribution of lithofacies (Cluff et al., 1981).

The predominantly black shales of the Blocher were probably deposited under anaerobic (1 ml dissolved \( O_2/1 H_2O \)) conditions, with a few periods of dysaerobic (between 1 and 1 ml dissolved \( O_2/1 H_2O \)) conditions represented by interbedded gray, bioturbated shales (Cluff et al., 1981). The alternating olive gray and black shales of the Selmier probably indicate deposition during fluctuating anaerobic and dysaerobic conditions (Cluff et al., 1981). The bioturbated greenish gray mudstones of the lower Grassy Creek may indicate a dysaerobic environment of deposition, but finely laminated carbonaceous black shales near the top of the formation indicate an anaerobic environment (Cluff et al., 1981).

Cluff et al. (1981) interpreted the geographic setting of the Wayne Co. location as deep basin. The Sullivan Co. site was interpreted as transitional between basin slope and deep basin during deposition of the New Albany Shale (Fig. 6) (Cluff et al., 1981).

Sedimentation Rates

Little can be said with certainty about absolute sedimentation rate during deposition of the New Albany Shale. Less can be said of possible fluctuations in sedimentation rates based on available data. It is reasonable to assume, however, that the overall sedimentation rate at Wayne Co. was relatively faster than at Sullivan Co.

Total thickness of the Blocher, Selmier, and Grassy Creek Shales at the Wayne Co. location is 224 feet. At Sullivan Co., the Blocher, Selmier, Grassy
Figure 6. Paleogeography of part of the Illinois Basin during deposition of the New Albany Shale.

Q = well location

(From Cluff et al., 1981.)
Creak and Hannibal shales have a combined thickness of 123 feet. The Hannibal Shale is indistinguishable from the underlying Grassy Creek at the Sullivan Co. well (Fig. 5 and Appendix). The entire New Albany Shale is also thicker at the Wayne Co. location. Figure 7 is a thickness profile of the New Albany Shale drawn through the Wayne and Sullivan Co. locations (also see Fig. 2).

Individual formations are also thicker at Wayne County. The thicknesses of the Blocker, Selmier and Grassy Creek Shales at Wayne Co. are 29, 62, and 133 feet respectively. At Sullivan Co., the Blocker, Selmier, and Grassy Creek—Hannibal Shales are 17, 23, and 85 feet thick, respectively (see Figs. 3, 4, 5, and Appendix). Considering formation boundaries as crude time lines, the Wayne Co. location had 1.7, 2.7, and 1.6 times faster sedimentation for the Blocker, Selmier, and Grassy Creek Shales, respectively, than the Sullivan Co. site.

There is no definite proof that the Wayne Co. locality had a continuously faster rate of sedimentation than the Sullivan Co. site. However, there is also no evidence of unconformities or substantial hiatuses in either of the cores (see Appendix). Therefore, it seems reasonable to assume that the Wayne Co. site experienced the faster overall rate of sedimentation during deposition of the New Albany Shale.
Figure 7. Thickness profile of the New Albany Shale between Wayne and Sullivan County cores.
CHAPTER 3
EXPERIMENTAL SECTION

**Sampling**

Samples used in this study were taken from cores by the Illinois State Geological Survey (ISGS) for a detailed report on the geology and geochemistry of the New Albany Shale Group in Illinois (Cluff et al., 1981). The two wells used for this study were the G. T. Jenkins #1 Simpson (SW-SE-SW 17-3S-8E Wayne Co., IL) and the Energy Res. Indiana #1 Phegly Farms (NW-NW-NE 14-6N-10W Sullivan Co., IN) (see Fig. 1). A description from Cluff et al. (1981) for the Wayne Co. core, and from the Indiana Geological Survey (Shaffer, IGS open file data) for the Sullivan Co. core are given in the Appendix.

Samples from several sections of these cores were received from the ISGS as coarse ground powders. The ISGS also supplied chemical analyses of all samples taken from the cores. Twenty samples were selected for isotopic analyses of pyritic sulfur based on pyrite content and stratigraphic distribution. Samples which contained sufficient carbonate for analyses (>3 wt.% CO₂) were analysed for δ¹³C and δ¹⁸O.

**Reporting Isotope Data**

Data for sulfur isotopes is reported in standard delta (δ) notation:

\[
δ^{34}S = \left( \frac{^{34}S / ^{32}S}{^{34}S / ^{32}S}_{\text{STD}} \right)_{\text{SMPL}} - \left( \frac{^{34}S / ^{32}S}{^{34}S / ^{32}S}_{\text{STD}} \right)_{\text{STD}} \times 1000
\]
The sulfur standard used is Canyon Diablo Troilite (CDT). Variation in the $^{13}$C/$^{12}$C and $^{18}$O/$^{16}$O of carbonates are reported in the $\delta$ notation relative to the PDB standard.

Fractionation between species ($A$) is reported as:

$$\delta_{A-B} = \delta_A - \delta_B.$$

For example, sulfur isotope fractionation between dissolved sulfate and the sulfide species produced by bacterial reduction of sulfate is expressed as:

$$\Delta^{34}S(\text{s}^- - \text{SO}_4^{2-}) = \delta^{34}S(\text{s}^-) - \delta^{34}S(\text{SO}_4^{2-}).$$

**Extraction of Pyritic Sulfur**

Extraction and isotopic analysis of pyritic sulfur was performed according to the procedure described by Westgate and Anderson (1982). Samples were ground to pass a 200 mesh sieve and dried to constant weight. A 2-5 g sample was then treated with HCl and heated to remove carbonates and acid soluble sulfides. Sulfur liberated as $\text{H}_2\text{S}$ was precipitated as $\text{CdS}$. None of the samples analysed had sufficient soluble sulfide to measure. The acid treated residue was filtered, rinsed, and dried to constant weight. It was then reacted with LAlH, dried tetrahydrofuran, and concentrated HCl. Sulfur liberated as $\text{H}_2\text{S}$ from the reduction of pyrite was precipitated as $\text{CdS}$, converted to $\text{Ag}_2\text{S}$, and stored. $\text{Ag}_2\text{S}$ was later combusted under vacuum. $\text{SO}_2$ liberated was collected and stored. This gas was analysed with a Varian MAT 250 isotope ratio mass spectrometer.
Westgate and Anderson (1982) report that contamination of pyrite by organic sulfur in coal samples is less than 3%, and isotopic variations of replicate extractions varied by ±0.07‰ to 0.33‰.

**Extraction of Carbonate Carbon**

Isotopic analyses of $^{13}\text{C}$ of the carbonate fraction were done on samples which contained more than 3 weight percent CO$_2$ as reported by the Illinois State Geological Survey. Samples were ground to pass a 200 mesh sieve and reacted with 100% H$_3$PO$_4$ under vacuum. CO$_2$ was extracted after the samples had reacted for twelve days. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ were measured on a MAT 250 isotope ratio mass spectrometer.
CHAPTER 4
RESULTS

The isotopic results from this study as well as IGGS data on sulfur and carbon contents are shown in Table 1.

Pyritic Sulfur

$\delta^{34}S$ values of pyritic sulfur vary by nearly 30°/oo. Samples from the Wayne Co. core show a larger variation (+3.8 to -24.6°/oo) than those from Sullivan Co. (-6.9 to -16.4°/oo). The average $\delta^{34}S$ for Wayne Co. samples is -11.4°/oo. $\delta^{34}S$ values averaged -14.8°/oo for Sullivan Co. samples. In Wayne Co. samples, pyrite content varied from 4.76 to 1.10 weight percent and averaged 2.26 weight percent. Sullivan Co. samples averaged 2.67 weight percent pyrite, and content ranged from 4.95 to 1.41 weight percent.

$^{13}C$ and $^{18}O$

The values for $\delta^{13}C$ and $\delta^{18}O$ are for total carbonate. Dolomite is the predominant carbonate except in the calcareous Blocher Shale (Cluff et al., 1981). In the Wayne Co. core $\delta^{13}C$ ranged from -0.24 to -11.72°/oo and averaged -7.05°/oo. $\delta^{18}O$ varied from -3.76 to -14.58°/oo and averaged -10.09°/oo. Values of $\delta^{13}C$ for Sullivan Co. samples varied from -5.29 to -2.09°/oo and averaged -3.48°/oo. $\delta^{18}O$ varied from -5.41 to -8.44°/oo and averaged -6.70°/oo.

Organic Carbon

The amount of organic carbon in samples varied by 9.46 weight percent as measured by the IGGS. The amount of organic carbon in Wayne Co. samples varies from 8.33 to 2.23 weight percent. Variation in the Sullivan Co. samples is from 9.38 to 2.93 weight percent. The average organic carbon content in Wayne
Co. samples is 5.10 weight percent. In Sullivan Co. samples, the average organic carbon content is 7.68 weight percent.
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CHAPTER 5

DISCUSSION

The Age Curve of Sulfur Isotopes in the Ocean

When sulfate minerals are precipitated they assume an isotopic composition close to that of the dissolved sulfate ion in the water from which they precipitated (Thode and Monster, 1963). Because time of mixing in the ocean is short in comparison to the residence time of sulfate ion, the isotopic composition of sedimentary sulfate in the rock record can be used to infer the isotopic composition of sulfate ion in ancient sea water. Claypool et al. (1980) used analyses of $\delta^{34}S$ from marine sulfate minerals to construct a revised curve of sulfur isotope variation of sulfate minerals precipitated in equilibrium with sea water through time (Fig. 8). The sulfate age curve shows that there have been several periods when the $\delta^{34}S$ of sulfate has undergone rapid change, such as during the Late Devonian. By using the sulfate-age curve, the extent of fractionation between marine sulfide and dissolved sulfate sulfur through time can be estimated.

Construction of the sulfate age curve, however, involved correlation of distant evaporite basins based on limited biostratigraphic evidence. Although Claypool et al. (1980) attempted to weigh the reliability of correlations when preparing the curve, uncertainties exist. Care must be taken when attempting definite correlation to the curve, especially during times of rapidly changing $\delta^{34}S$ values (Claypool et al., 1980). The age curves for the Upper Devonian are superimposed on the stratigraphic units analyzed here in Figures 8c and d.

Bacterial Sulfate Reduction

In the absence of oxygen, certain bacteria reduce sulfate ion to sulfide. The reaction describing sulfate reduction can be written as:

\[
2\text{H}_2\text{S} + 3\text{O}_2 \rightarrow 2\text{H}_2\text{O} + 2\text{S} + 6\text{H}^+. 
\]
Figure 8a. Sulfate-age curve.
(From Claypool et al., 1980.)
Figure 8b. Sulfate-age curve for the Devonian.
(From Claypool et al., 1981.)

Figure 8c. Sulfate-age curve superimposed on stratigraphy of the Wayne County core.
Figure 8d. Sulfate age curve superimposed on stratigraphy of the Sullivan County core.
SO$_4^{2-}$ + 2CH$_2$O + 2HCO$_3^-$ + H$_2$S.

The byproducts of this reduction react with iron in the sediment to form pyrite (FeS$_2$). Today, bacterial reduction of sulfate occurs in anoxic, organic rich sediments.

The most important factors influencing the rate of bacterial reduction are amount and type of organic matter in the sediment (Kaplan and Rittenburg, 1964). Harrison and Thode (1958) demonstrated that reduction rate is independent of sulfate concentration above a limiting concentration of about 10 mM. Decreased temperature decreases reduction rate (Kaplan and Rittenburg, 1964; Harrison and Thode, 1958), but the effects of pressure on reduction rates are poorly understood.

Because rate of sulfate reduction is related to supply of organic matter, Goldhaber and Kaplan (1975) have suggested that bacterial reduction rate is directly related to sedimentation rate in modern marine sediments. Studies of marine sediments in several areas have shown that increased sedimentation rate is positively related to the rate of sulfate reduction (Berner, 1977; Goldhaber and Kaplan, 1975).

A consequence of bacterial sulfate reduction is the fractionation of sulfur isotopes. It is well documented that $^{32}$S is concentrated in the reduced form (Harrison and Thode, 1958; Thode et al., 1961; Kaplan and Rittenburg, 1964). The extent of fractionation is largely controlled by the rate of bacterial reduction (Harrison and Thode, 1958; Kaplan and Rittenburg, 1964; Chambers et al., 1975). Fractionation of sulfur isotopes between sulfate and sulfide species decreases with increased sedimentation rate (Goldhaber and Kaplan, 1975; Berner, 1977).
Other environmental conditions may also influence the total fractionation observed in marine sediments. Goldhaber and Kaplan (1980) noted that fractionation is enhanced if sulfate continuously diffuses into the sediment. They argued that $^{32}\text{S}$ is preferentially added to the zone of bacterial sulfate reduction by diffusion. Sulfate added to the sediment in this manner had a $\delta^{34}\text{S}$ of -4.5‰ as compared to +24‰ of sea water. This light sulfate would be subjected to further fractionation by sulfate reducing bacteria.

**Carbon Isotope Variations**

Carbonate in the samples analysed occurs as rhombo, detrital silts, and diagenetic fracture filling (see Appendix). It is unclear whether $\delta^{13}\text{C}$ of these samples reflects $\delta^{13}\text{C}$ of sea water during deposition of the New Albany Shale. The $\delta^{13}\text{C}$ values from the samples, then, cannot be used to examine contemporaneous variations in $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ in order to estimate mass fluxes of sulfur and carbon between reduced and oxidised phases (Carrels and Lerman, 1981).

**Sulfur and Carbon Content Relationships**

Figure 9 shows a plot of organic carbon against pyrite content in the samples. The observed negative relationship is similar to that noted by Shaffer (Indiana Geological Survey, open file data) and others (Anderson, unpublished data). This may be the result of increased amounts of metabolizable organic matter allowing increased duration of sulfate reduction and hence pyrite deposition.

**Observed Variations of $\delta^{34}\text{S}$**

Values of $\delta^{34}\text{S}$ in both cores tend to be more positive near the base than higher in the section (Fig. 10). Shaffer (1982) also noted this trend in
Figure 9. Variation of pyrite content with organic carbon content.
Figure 10a. Variation of $\delta^{34}S$ with depth in the Wayne County core.

Figure 10b. Variation of $\delta^{34}S$ with depth in Sullivan County core.
\( \delta^{34} \) in the New Albany Shale from analyses of cores in Indiana. \( \delta^{34} \) of both cores are heaviest at the base of the Bloomer Shale and become rapidly lighter up-section. \( \delta^{34} \) reaches a minimum value in the Selmer Shale in both cores. Lighter \( \delta^{34} \) values are recorded at the top of the Sullivan Co. core, but those samples are probably Mississippian in age (Cluff et al., 1981). At the base of the Grassy Creek Shale, \( \delta^{34} \) returns to heavier values. In the Sullivan Co. core, \( \delta^{34} \) values remain constant at about -15°/oo. However, \( \delta^{34} \) values in the Grassy Creek from the Wayne Co. core become 20°/oo more positive than in the Selmer Shale, and then decrease to about -15°/oo at the top of the section.

**Estimated Variations of \( \delta^{34} \) (pyrite-sea water)**

Fractionation (\( \Delta^{34} \)) between dissolved sulfate in sea water and pyrite produced by bacterial reduction of sulfate can be estimated by superimposing the sulfate-age curve on a plot of \( \delta^{34} \) against depth (Fig. 11). The uppermost samples from the Sullivan Co. core have not been included because of their suspect ages. The curves of \( \Delta^{34} \) against depth show striking similarity. This similarity, however, is due in part to the large variations of \( \delta^{34} \) with depth (30°/oo for the Wayne Co. core) compared to the sulfate-age curve (about 4°/oo). If correlation to the sulfate-age curve were changed, the \( ^{34}S \) curve would remain about the same. However, the \( ^{34}S \) curves illustrate two points. First, there were large variations in the extent of fractionation during deposition of the New Albany Shale. Second, the sulfate age curve is apparently inversely related to the \( ^{34}S \) curve, as shown by comparing Figure 11a to 11c. This may indicate an inverse relationship between sulfate and sulfide deposition during the Late Devonian.
Figure 11a. Variation of $\Delta^{34}S$ with depth in the Wayne County core. Lines show estimated error from sulfate-age curve.
Figure 11b. Variation of $\Delta^{34}S$ with depth in Sullivan County core. Lines show estimated error from sulfate age curve.

Figure 11c. Sulfate-age curve for the Devonian. Compare to 11a and b. (From Clapp et al., [Year].)
A possible explanation for the large discrepancy between $\delta^{34}S$ variation and the sulfate-age curve is that the Illinois Basin did not have a large degree of contact with the world ocean during deposition of the New Albany Shale. Similar interpretations have been made to explain observed sulfur isotope variations in other black shales. Maynard (1980) observed progressively heavier $\delta^{34}S$ values with increasing stratigraphic elevation in Devonian black shales from the Appalachian Basin. He interpreted this as evidence of progressive closing of the basin through the Devonian.

In such a model, dissolved sulfate in the restricted basin would become increasingly enriched in $^{34}S$ as bacteria preferentially reduced the light isotope in sulfides. However, this is not consistent with observed $\delta^{34}S$ trends in the New Albany Shale. As noted earlier, $\delta^{34}S$ for both cores is heaviest in the bottom-most shales. If the Illinois Basin had been closed for a long period of time prior to deposition of the Blocher Shale, conditions other than normal marine should have prevailed during deposition of the laterally continuous limestones of the Lingle Formation (Cluff et al., 1981). The fauna of the Lingle Formation, however, has not been noted as representing other than normal marine conditions (Collinson and Atherson, 1975; North, 1969). There is no obvious isotopic evidence to disprove progressive closing of the basin during deposition of the Grassy Creek. Such an event could provide a mechanism for driving $\delta^{34}S$ to the more positive values observed at the base of the Grassy Creek Shale.

$\delta^{34}S$ in the Blocher Shale

There are several possible explanations for the high $\delta^{34}S$ values observed in the Blocher Shale. Lowering the stratigraphic position of the sulfate-age
curve relative to the stratigraphy of the New Albany Shale is the first. If this were the case, the maximum $\delta^{34}S$ in the sulfate curve would correlate with the heaviest observed sulfide values. As discussed earlier, there is some doubt as to the exact stratigraphic placement of the sulfate-age curve. However, the maximum sulfate curve values are almost certainly placed in the Frasnian (Claypool et al., 1980). The placement of the Givetian-Frasnian boundary for the Illinois Basin is, if anything, high; and the Blocher Shale may not be entirely Givetian in age (Guiff et al., 1981). Therefore, uncertain correlation of the sulfate age curve is a possible explanation for the otherwise anomalous $\delta^{34}S$ values observed in the Blocher Shale.

A second possible explanation for the heavy $\delta^{34}S$ values at the base of the Blocher Shale is an increased rate of bacterial reduction during deposition of the Blocher Shale. As mentioned earlier, rapid reduction of sulfate would decrease fractionation between $^{34}S$ and $^{32}S$ (Goldhaber and Kaplan, 1975; Berner, 1978). Figure 12 shows the vertical changes in carbon content. These data show that the Blocher Shale does not contain an unusually large content of organic carbon. Since rate of bacterial reduction is heavily dependent on the amount of organic matter present (Goldhaber and Kaplan, 1975), the Blocher Shale should not have experienced an exceptionally fast rate of sulfate reduction. The high carbonate content of the Blocher Shale may have affected rate of sulfate reduction (and so extent of fractionation) by altering the pH of the sediments. However, Chambers et al. (1975) did not note significant change in bacterial fractionation of sulfur in response to pH.

**Relation of $^{34}S$ to Organic Carbon Content**

As stated above, in modern marine sediments sulfur isotope fractionation decreases with increasing metabolizable organic carbon (Netrubin and Share,
Figure 12a. Variation of organic carbon content with depth, Wayne County core.

Figure 12b. Variation of organic carbon content with depth, Sullivan County core.
1958; Kaplan and Rittenburg, 1964; Chambers et al., 1975). When Δ³⁴S is plotted against organic carbon content, Δ³⁴S decreases with increasing carbon (Fig. 13). Shaffer (Indiana Geological Survey, open file data) has noted the same trend in New Albany Shale cores from Indiana. The relationship between Δ³⁴S and organic carbon content, however, is not clear (Fig. 14).

The relationship between Δ³⁴S and organic carbon content could be explained if increased amounts of organic carbon allowed extended periods of bacterial sulfate reduction in an open system. As described earlier, fractionation of sulfur isotopes remains high if the reducing bacteria are exposed to a continuously replenished supply of sulfate (Goldhaber and Kaplan, 1980). If diffusion of sulfate into the sediment continued throughout the reduction process, large amounts of organic matter could allow for extended periods of bacterial reduction at a constant rate. In such a system, Δ³⁴S would be expected to decrease with increased amounts of organic matter.

Δ³⁴S Variation Against Inferred Sedimentation Rate

As discussed above, in modern marine sediments, the fractionation of sulfur isotopes by bacterial reduction decreases with faster sedimentation rates (Goldhaber and Kaplan, 1975). A faster sedimentation rate at the Wayne Co. location would lead to smaller Δ³⁴S and more positive Δ³⁴S values (see Figs. 10 and 11). Variations from expected values could represent alternating periods of very rapid and slow deposition at Wayne Co., (especially during deposition of the Grass Creek) while the Sullivan Co. site experienced a relatively constant, moderate rate of sedimentation.

The large range of values for the Wayne Co. samples may also be related to the geometry of the basin. The Wayne Co. site is slightly south and west of
Figure 13a. Variation of $\delta^{34}S$ with organic carbon content, Wayne County core.

Figure 13b. Variation of $\delta^{34}S$ with organic carbon content, Sullivan County core.

Figure 14a. Variation of $\Delta^{34}S$ with organic carbon content, Wayne County core. Lines show estimated error from sulfate-age curve.

Figure 14b. Variation of $\Delta^{34}S$ with organic carbon content, Sullivan County core. Lines show estimated error from sulfate-age curve.
locally thicker shales (Fig. 7). Some factors influencing sulfate reduction may have been affected by the increased sedimentation there. In particular, the large range of $\delta^{34}S$ values may record variations in the reducing environment especially at such a possibly restricted site.

**Effect of Bioturbation of Sulfur Isotope Composition**

Bioturbation of marine sediments would have two contrasting effects on sulfur isotope compositions. First, bioturbation would decrease the organic carbon content of the sediment. This would decrease the rate of bacterial sulfate reduction and extent of fractionation. However, bioturbation would also mix the sediment and increase diffusion of sulfate to reducing bacteria, increasing isotope fractionation (Goldhaber and Kaplan, 1980). Figure 15 shows variations of $\delta^{34}S$ and $\Delta^{34}S$ with bioturbation.

**Variation of $^{34}S$ with Sulfur Content**

As shown in Figures 16 and 17, neither $\delta^{34}S$ nor $\Delta^{34}S$ appear to be related to pyrite content in the samples. The pyrite content of the samples is higher than can be accounted for by simple burial of dissolved sulfate with interstitial pore water (Goldhaber and Kaplan, 1980). This would argue that the reducing bacteria were exposed to a constant supply of sulfate. If sulfate supply had been restricted, $\delta^{34}S$ would increase as more pyrite was formed, since bacteria would be forced to reduce $^{34}S$ enriched residual sulfate as reduction and fractionation continued.
Figure 15a. Variation of $\delta^{34}S$ with bioturbation, Wayne County core.
Figure 15b. Variation of $\Delta^{34}S$ with bioturbation, Wayne County core.
Figure 16a. Variation of $\delta^{34}S$ with pyrite content, Wayne County core.

Figure 16b. Variation of $\delta^{34}S$ with pyrite content, Sullivan County core.
Figure 17a. Variation of $\Delta^{34}S$ with pyrite content, Wayne County core. Lines show estimated error from sulfate-age curve.

Figure 17b. Variation of $\Delta^{34}S$ with pyrite content, Sullivan County core. Lines show estimated error from sulfate-age curve.
CHAPTER 6
CONCLUSIONS

As shown in Figures 10 and 11, there are similar trends of sulfur isotope fractionation in the two cores studied. However, samples from Wayne Co. showed much greater variation of sulfur isotope fractionation. The observed differences in fractionation cannot be explained by differences in fractionation rates.

Values of $\delta^{34}S$ and organic carbon content apparently show an inverse relationship (Fig. 12), but $\delta^{34}S$ values do not (Fig. 13). This relationship may be explained if increased amounts of organic matter allowed longer periods of bacterial sulfate reduction with a continuous supply of sulfate.

These results suggest that factors which control bacterial sulfate reduction in modern sediments are different than those which operated during deposition of the New Albany Shale.
**APPENDIX**

**CORE DESCRIPTIONS**

**PART 1. Wayne County Core (from Cluff et al., 1981)**

**NAME:** Gordon T. Jenkins #1 Simpson, Wayne County, Illinois

**LOCATION:** SW1/4 SE1/4 SW1/4, Sec. 17, T.3 S., R. 6 E., Wayne County, Illinois (API Number 1219129436)

**ELEVATION:** 387 feet (118.0 m) above m.s.l. (kelly bushing)

**DESCRIPTION:** J. A. Lineback and R. M. Cluff, Oct. 1979

<table>
<thead>
<tr>
<th>Depth</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>New Albany Shale Group</strong></td>
<td></td>
</tr>
<tr>
<td>HANNIBAL-SAVARTON SHALES</td>
<td></td>
</tr>
<tr>
<td>5041.1 to 5041.5 ft</td>
<td>Shale, light olive-gray (5Y6/1), noncalcareous, bioturbated with small Zoophycos burrows (Jacobs Chapel Bed)</td>
</tr>
<tr>
<td>5041.1 to 5042.7 ft</td>
<td>Shale, brownish black (5YR2/1), noncalcareous, very thin even parallel laminations in lower part, small burrows penetrate top from overlying gray-shale (Henryville Bed)</td>
</tr>
<tr>
<td>5042.7 to 5042.8 ft</td>
<td>Shale, dark brownish gray (5YR3/1), with large phosphatic nodules (Falling Run Bed)</td>
</tr>
<tr>
<td>5042.8 to 5043.2 ft</td>
<td>Shale, brownish black (5YR2/1) as above</td>
</tr>
<tr>
<td>5043.2 to 5043.3 ft</td>
<td>Shale, brownish black (5YR2/1) as above</td>
</tr>
<tr>
<td>5043.3 to 5051.2 ft</td>
<td>Shale, olive-gray (5Y4/1) grading downward into olive-black (5Y2/1), massive, calcareous in upper part, brachiopods scattered throughout and most abundant in lower portion; scoured basal contact with concentration of brachiopod shells</td>
</tr>
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<td></td>
</tr>
</tbody>
</table>
5051.2 to 5074.0 ft
Shale, brownish black (5YR2/1), noncalcareous, irregularly spaced thin pyritic laminae, some layers of slightly lighter colored shale; several mineralized fractures between 5066 and 5070 ft.

5074.0 to 5097.0 ft
Shale, brownish black (5YR2/1), very thin dolomitic and calcareous laminae, pyritic, few fractures; silty (?) pyritic layer 0.2 ft thick at 5077.1 ft; core badly broken and fractured below 5087 ft; footages near base are approximate; fractures closely spaced and mineralized below 5095 ft.

5097.0 to 5136.0 ft
Shale, brownish black (5YR2/1), pyritic, few irregularly spaced very thin dolomitic laminae, noncalcareous, scattered short high-angle fractures; bottom one foot highly broken.

5136.0 to 5149.5 ft
Shale, brownish black (5YR2/1), slightly pyritic, very thin faint dolomitic laminae, two thin beds of dark olive-gray shale (5Y4/1), long near-vertical fracture in lower part.

5149.5 to 5162.0 ft
Shale, brownish black (5YR2/1) to olive-black (5Y2/1), with many very thin beds of olive-gray shale (5Y4/1) with burrows extending down from bases into black shale; pyritic and thin dolomitic laminae common; bottom three to four feet highly shattered and fractured.

5162.0 to 5178.0 ft
Shale, brownish black (5YR2/1), pyritic, few thin dark olive-gray to olive-black beds; bottom four feet highly broken and fractured.

5178.0 to 5184.5 ft
Shale, brownish (5YR2/1) with thin interbeds of olive-gray (5Y4/1) shale, discontinuous, even, very thin laminae, gray shales slightly bioturbated, several irregular dolomitic siltstone lenses; discontinuous vertical fractures throughout.

5184.5 to 5199.0 ft
Shale, olive-gray (5Y4/1) to dark olive-gray (5Y2/1), moderately bioturbated, moderately bioturbated; interbeds of olive-gray (5Y4/1) shale; black shales with many beaches and bioturbated casts; bottom two feet highly shattered and bioturbated, several irregular dolomitic siltstone lenses; discontinuous vertical fractures throughout.

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GRASSY CREEK SHALE

SHAPIER SHALE

5124.9 to 5185.0 ft
Shale, olive-gray (5Y4/1) to dark olive-gray (5Y2/1), moderately bioturbated and moderately bioturbated; interbeds of olive-gray (5Y4/1) shale; black shales with many beaches and bioturbated casts; bottom two feet highly shattered and bioturbated, several irregular dolomitic siltstone lenses; discontinuous vertical fractures throughout. Major vertical fracture from 5124.9 to 5185.0 ft.
5199.0 to 5218.5 ft
Shale, brownish black (5YR2/1) to olive-black (5Y2/1), widely spaced and irregular discontinuous even-thick dolomite laminations, very few thin beds of lighter colored shale; several zones of closely spaced even-parallel pyritic laminae

5218.5 to 5220.9 ft
Shale, brownish black (5YR2/1) interbedded with olive-gray (5Y4/1), widely spaced even very thin laminae, pyritic; small pyritic burrows in gray shales

5220.9 to 5224.5 ft
Shale, brownish black (5YR2/1) to olive-black (5Y2/1), pyritic with numerous nodules and thick laminae

5224.5 to 5229.8 ft
Shale, olive-gray (5Y4/1 to 5Y3/1), indistinctly bedded to massive, moderately bioturbated, few widely spaced thin pyrite laminations, many small pyrite nodules, indistinct beds of slightly darker shale

5229.8 to 5236.9 ft
Shale, olive-black (5Y2/1 to 5Y3/1), few thin even-parallel dolomitic and pyritic laminae, numerous irregular pyrite nodules

5236.8 to 5246.3 ft
Shale, brownish black (5YR2/1), even-parallel and discontinuous even very thin laminae, pyritic with scattered nodules, noncalcareous

BLOCHNER SHALE

5246.3 to 5273.1 ft
Shale, brownish black (5YR2/1), even-parallel very thin pyritic laminations, highly calcareous, very sharp upper contact; several calciretic beds up to 5 cm thick and slightly lenticular or cross-beded (at 5250.1 ft, 5253.0 ft, 5259.8 ft, 5261.5 ft, 5265.9 ft, and 5273.7 ft); shale is slightly more massive in lower part and is speckled with microfossils (?); major vertical fractures from 5246-5252 ft and 5261-5275.5 ft
**PART 2. Sullivan County Core (from Shaffer, Indiana Geological Survey, open file data)**

**NAME:** Energy Resources of Indiana, Inc., Phagly Farms, Inc. #1

**LOCATION:** NW NW NE Sec 14 6W 10W, Sullivan County, Indiana

**ELEVATION:** 430 feet (ground level)

**DESCRIPTION:** Nelson R. Shaffer

Mississippian-Devonian System

New Albany Shale, 125.3 ft cored

<table>
<thead>
<tr>
<th>Unit</th>
<th>Depth</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2304.3 to 2305.5 ft</td>
<td><strong>Grassy Creek Member</strong> Shale, black, carbonaceous, thin bedded with silt bands at .1' below contact, pyrite abundant, as disseminated crystals and in discrete thin beds, fracture filled with white calcite.</td>
</tr>
<tr>
<td></td>
<td>2305.9 to 2305.9 ft</td>
<td>Sample removed</td>
</tr>
<tr>
<td></td>
<td>2306.9 to 2306.1 ft</td>
<td>Shale, black with thin beds of silt, carbonates and pyrite; diagonal fractures; hard spherical bodies with calcite fill and pyrite fill out bedding; white carbonate replacement; filled burrows.</td>
</tr>
<tr>
<td></td>
<td>2308.1 to 2312.4 ft</td>
<td>Shale, as above but with silt bands and discrete vitrinite fragments. Silt and pyritic bands; bedding planes at 2310.4 has numerous plant fragments, conodonts, lingula, and spores; pyrite filled burrow 2310.8; fractures continue.</td>
</tr>
<tr>
<td></td>
<td>2312.4 to 2315.3 ft</td>
<td>Shale, like unit 14, but with numerous pyrite masses and few thin silt and pyrite beds. Silt beds with pyrite.</td>
</tr>
<tr>
<td></td>
<td>2319.3 to 2325.7 ft</td>
<td>Sample removed</td>
</tr>
<tr>
<td></td>
<td>2326.7 to 2329.4 ft</td>
<td>Shale, black with prominent silt and pyrite beds having pyritous bedding and thin pyrite horizons; marginal structures.</td>
</tr>
</tbody>
</table>
19 2519.4 to 2521.2 ft  Shale, black pyrite lenses, silt and pyrite bed 2519.1.

20 2521.2 to 2521.5 ft  Sample removed

21 2521.5 to 2524.2 ft  Shale, black, thin bedded as above; pyrite silt and calcite beds; diagonal fracture; mineralized vertical fracture.

22 2524.2 to 2527.9 ft  Shale as above but characterised by angular pyrite masses, sherd like in form. Also contains white rhombo of dolomite. Pyrite lamellae more numerous downward; mineralised vertical fracture continues downward; bedding plane with spores 2527.35.

23 2527.9 to 2528.2 ft  Sample removed

24 2528.2 to 2530.7 ft  Shale, black, compact with numerous thin discontinuous pyrite lamellae, few thin white silt beds; coalified wood fragments parallel to bedding; many large pyrite nodules; lenses of coosue plant fragments.

25 2530.7 to 2531.4 ft  Shale as above but rich in spore cases, very few pyrite lamellae, no pyrite masses.

26 2531.4 to 2535.4 ft  Shale like unit 24 with abundant pyrite lamellae, massive pyrite, spores persist.

27 2535.4 to 2536.3 ft  Shale like 24 but lacking large pyrite masses; silt bed with pyrite filled burrows; vitrain on bedding, small pyrite beds.

28 2536.5 to 2536.9 ft  Sample removed

29 2536.9 to 2539.8 ft  Shale, as unit 27

30 2539.8 to 2542.4 ft  Shale, black to dark gray with few silt and pyrite beds, many lamellae, pyrite masses, silt and pyrite beds.

31 2542.4 to 2545.1 ft  Shale black with abundant disseminated pyrite; pyrite masses, lamellae, silt beds.

32 2545.1 to 2547.1 ft  Shale, black, rich in spores, less pyrite, slight brown tone.

33 2547.1 to 2547.5 ft  Sample removed
34  2547.5 to 2549.2 ft  Shale, black with few irregular very dark grayish brown beds, abundant thin gray carbonate lamellae, numerous spores decreasing downward.

35  2549.2 to 2549.7 ft  Sample removed

36  2549.7 to 2554.3 ft  Shale, dark gray with more brownish material, abundant spores, pyrite masses and lamellae.

37  2554.3 to 2554.8 ft  Sample removed

38  2554.8 to 2561.8 ft  Shale, black, slightly brown, contains spores (abundant locally) but decreasing downward to 2558.7; pyrite masses and lamellae, silt beds.

39  2561.8 to 2565.2 ft  Shale, dark gray brown with numerous dark patches and abundant disseminated pyrite, but few large nodules. Silt and pyrite beds, random mineralized diagonal fractures.

40  2565.2 to 2565.6 ft  Sample removed

41  2565.6 to 2570.3 ft  Shale, like 39 but black material dominates; pyrite nodules and burrow fills; diagonal fractures filled with carbonates and minor blue unknown mineral.

42  2570.5 to 2571.5 ft  Sample removed

43  2571.5 to 2573.3 ft  Shale, like 41

44  2573.3 to 2575.6 ft  Sample removed

45  2575.6 to 2577.7 ft  Shale, like 41

46  2577.7 to 2580.3 ft  Shale, like 41 but with abundant spores and little pyrite.

47  2578.3 to 2579.0 ft  Sample removed

48  2579.0 to 2583.2 ft  Shale, like above, but with more silt beds and blacker; dark brown beds.

49  2583.2 to 2585.6 ft  Sample removed

50  2585.6 to 2589.5 ft  Shale, mostly black with dark brown beds, pyrite masses and silt beds.
**SWEETLAND CREEK MEMBER (SELMIFER SHALE)**

51  2589.5 to 2590.6 ft  
Shale, olive gray with black interbeds, abundant pyrite, numerous plant fragments; bottom 1-2 cm, pink-brown dolomite, lower boundary irregular and pyrite rich.

52  2590.6 to 2590.8 ft  
Shale, like 50

53  2590.8 to 2591.6 ft  
Argillaceous dolomite, light gray, finely crystalline, pyritiferous, with irregular white calcite fossil fillings. Thin green clay beds at base and top. Unit is lens-shaped.

54  2591.6 to 2592.1 ft  
Shale, dark olive gray, beds dip parallel to dolomite lens.

55  2592.1 to 2594.5 ft  
Shale, black to dark brown with numerous lighter colored irregular dolomite rich beds.

56  2594.5 to 2595.3 ft  
Shale alternating black to dark brown, lacks light colored dolomite lenses of above, pyritic.

57  2595.3 to 2595.7 ft  
Sample removed

58  2595.7 to 2602.7 ft  
Shale, black to dark brown, pyrite increasing downward, fewer silt beds; some brown beds.

59  2602.7 to 2604.0 ft  
Sample removed

60  2604.0 to 2611.6 ft  
Shale, dark brown with black beds, disseminated carbonate and thin silt and carbonate beds, massive pyrite and pyrite lamellae; vertical fracture, mineralized in part.

61  2611.6 to 2612.7 ft  
Shale, like 60, with numerous pyrite bodies that cut across bedding; carbonate and silt band.

**BLOOMER SHALE**

62  2612.7 to 2613.2 ft  
Shale, black very fine grained, above silty luster on bedding, large pyrite nodules; diagonal fractures.

63  2613.2 to 2618.6 ft  
Shale, black with few brown beds, numerous pyrite lamellae; pyrite masses, carbonate and silt beds.
64 2618.8 to 2619.2 ft

Dolomite, fine grained, dark gray brown, argillaceous, with pyrite, lens shaped.
REFERENCES


