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# SULFUR ISOTOPES OF IRON SULFIDES IN DEVONIAN-MISSISSIPPIAN SHALES OF THE APPALACHIAN BASIN: CONTROL BY RATE OF SEDIMENTATION

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ABSTRACT. In modern sediments, the isotopic composition of sulfur in iron sulfides appears to be controlled by sedimentation rate and by degree of contact of the basin with open seawater. A relationship is derived between $\delta^{34}S$ and sedimentation rate, which is then applied to data from ancient rocks. Sulfur isotopes in the Kupferschiefer seem to be controlled by the degree of contact of the basin with the open ocean rather than by rate of sedimentation. In the Devonian-Mississippian shales of the Appalachian Basin, on the other hand, there is a clear-cut correspondence between sulfur isotopes and inferred relative rates of sedimentation. Using the equation from recent sediments gives reasonable values for the relative rates of deposition of the various sedimentary units, but the absolute values seem too high by a factor of about five. There are several possible explanations for this discrepancy, but choosing among them requires further data from recent sediments. The relative curve, however, can still be used, if similar samples are compared.

## INTRODUCTION

The rate of sedimentation is one of the most important variables determining the sedimentary structures, facies geometry, and even geochemistry of sediments (Curtis, 1977). It is a commonly measured variable in modern sediments but is very difficult to estimate in ancient rocks. This paper proposes a technique for approximating relative sedimentation rates in shales using sulfur isotopes.

Sulfide minerals that form during or shortly after deposition in modern sediments, that is by way of bacterial sulfate reduction (Berner, 1971, p. 132), appear to show a relationship between sulfur isotopes and sedimentation rate. It has been observed that sediments deposited at high rates of sedimentation are associated with relatively less negative values of $\delta^{34}S$ than those formed at slow sedimentation rates (Goldhaber and Kaplan, 1975). This relationship can be explained by the fact that the rate of sulfate reduction by bacteria increases with increasing sedimentation rate coupled with the fact that at high reduction rates, bacteria perform less isotope fractionation and consequently produce sulfides with less negative $\delta^{34}S$ values. In this paper, a quantitative expression for this relationship is derived. Then sulfur isotope data from two ancient black shale deposits, the Kupferschiefer and the Devonian shales of the Appalachian Basin, are evaluated using this expression.

## METHODS

The isotope data reported here is expressed in the standard delta notation using troilite of the Canon Diablo meteorite as the primary standard:

$$\delta^{34}S \text{ sample} = 1000 \times (^{34}S/^{32}S \text{ sample} - \delta^{34}/^{32}S \text{ standard})/^{34}S/^{32}S \text{ standard},$$

with $\delta$ values reported in per mil (‰). The Devonian-Mississippian sam-

ples were analyzed commercially by Geochron Laboratories, Cambridge, Mass.

Most of the samples used were from outcrops and were chosen only from fresh exposures. Most of the samples were nodules >1 cm in diameter. For each sample, 25 to 50 g of sulfide was ground to <100 mesh and washed with dilute HCl and then water. Finally a bromoform separation was used to remove any remaining light mineral impurities. The isotope determinations were made using a Micromass 602D mass spectrometer with a heated inlet. The sulfur isotopes were measured on $SO_2$ gas, which was obtained by combusting the sulfide sample in an oxygen stream at 1300°C. The resulting $SO_2$ gas was trapped using liquid $O_2$. In carbon-containing samples, such as kerogen isolates, carbon is removed by trapping the $SO_2$ using frozen n-pentane, then pumping off $CO_2$ gas.

## DATA FROM RECENT SEDIMENTS

There is an extensive literature on the geochemistry of sulfur in recent sediments, which has been reviewed by Goldhaber and Kaplan (1974). The same authors have also described in some detail the isotope geochemistry of sulfur in recent sediments (Goldhaber and Kaplan, 1975). They found that there was a correlation between sedimentation rate and $\delta^{34}S$ values of sulfides, but they consider the ultimate control over $\delta^{34}S$ in sulfides to be the rate of sulfate reduction, which is itself proportional to the sedimentation rate. $\delta^{34}S$ appears to be linearly related to the log of the sulfate reduction rate, R (fig. 1), although more data at high reduction rates are needed. The resulting empirical relationship is:

$$\log R = 0.084\ \delta^{34}S - 1.32. \quad (1)$$

Berner (1978) has recently investigated the relationship of sulfate reduction to sedimentation rate in recent sediments. He found (p. 497),

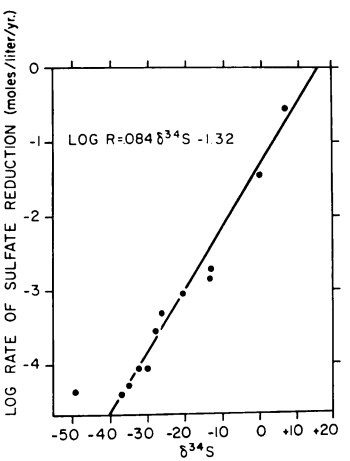


Fig. 1. Relationship between sulfate reduction rate and $\delta^{34}S$. Data from Goldhaber and Kaplan (1975, fig. 8).

in agreement with the earlier work of Toth and Lerman (1977), the relation

$$k = A\omega^2$$

where k is the first-order rate constant for organic matter decomposition as a result of sulfate reduction, $\omega$ is the sedimentation rate (in cm/yr), and A is a constant, found to be 0.04 yr • $cm^{-2}$. The k of this equation can be related to the R of Goldhaber and Kaplan (1974) by

$$R = LkG^\circ$$

(Goldhaber and Kaplan, 1974, p. 523; Berner, 1972, p. 351), where L is a stoichiometric factor relating organic matter to sulfate reduction, and $G^\circ$ is the initial concentration of utilizable organic carbon, shown by Berner (1978) to be nearly constant in recent sediments from reducing environments. From Berner (1978, p. 497), $L = 1/2$ and $G^\circ = 0.25$ moles • $liter^{-1}$. Thus

$$R = LG^\circ A\omega^2$$

or

$$R = 5 \times 10^{-3}\omega^2. \tag{2}$$

Combining (1) and (2) give a relationship for sulfur isotopic composition as a function of sedimentation rate (in cm/yr):

$$\delta^{34}S = 23.8 \log \omega - 11.6. \tag{3}$$

This equation can be generalized to cover situations other than modern seawater by using the variable $\Delta\delta^{34}S$, which is the difference between $\delta^{34}S$ of the $SO_4^{--}$ and the resulting sulfides. For modern-day seawater $\delta^{34}S$ of the sulfate is about +20.0 per mil (Holser and Kaplan, 1966) so that (3) becomes

$$\Delta\delta^{34}S = 31.6 - 23.8 \log \omega. \tag{4}$$

Because in ancient rocks $\delta^{34}S$ can be directly measured, but $\omega$ only inferred, it is best to recast $\Delta$ as the independent variable:

$$\text{Log } \omega = 1.33 - 0.042\ \Delta\delta^{34}S. \tag{4a}$$

Remember that this relationship is empirical and that some of the terms treated as constants, such as $G^\circ$ and A, may in fact have been different at earlier times in the Earth's history.

From only a few modern basins do we have sulfur isotope data to test this relationship directly (fig. 2). Note that the predicted behavior holds fairly well for the higher sedimentation rates but fails at rates less than 0.1 cm/yr. Apparently isotope fractionation approaches a limit at these slow rates.

Hartman and Nielsen (1968) have also reported a qualitative relationship between $\delta^{34}S$ and sedimentation rate in the Baltic Sea. Areas with a high sedimentation rate average −21‰, whereas those with low rates average −31‰. The corresponding sedimentation rates from eq (3) are 0.40 and 0.14 cm/yr, consistent with reported values of 0.25 to 0.10 cm/yr (Reineck, 1960, table 1) for the Baltic.

There is also evidence from ancient rocks for a control of sulfur isotopes by sedimentation rate (Ronov and others, 1974). These workers described an association of more positive $\delta^{34}S$ values with higher sedimentation rates (fig. 3). If the data are plotted as $\Delta\delta^{34}S$, the trend is similar to the recent sediments, but note that although the slope value of −0.042 from eq (4A) can be used, there is a completely different intercept. The rates in figure 3 would be smaller than those in figure 2 by a factor of about fifty. Some of this difference is due to compaction, but most is due to the fact that the data from recent sediments are "instantaneous" rates, whereas the rates in the Russian data are integrated over complete stratigraphic units and so include the hiatuses, which take up the bulk of geologic time.

The expression in (4) is the quantification of what we might call the reduction-rate hypothesis. There is also a closed-system versus open-system hypothesis, summarized by Schwarz and Burnie (1973). Basically, open systems are those that maintain some contact with an external reservoir of sulfur (usually seawater), whereas closed systems do not. Sulfate reduction goes to completion in a closed system in a kind of batch process, and the resulting $\delta^{34}S$ of the sulfides must be the same as that of the original sulfate. In an open system, on the other hand, the bacteria can select the light isotope ($^{32}S$), producing a considerable fractionation relative to the original sulfate. Based on data from sulfide ore bodies, Schwarz and Burnie argued that those sulfide deposits that form in open system, having free contact with seawater $SO_4^{--}$, should have $\delta\Delta^{34}S$ values of 50‰. In contrast, closed systems should have $\Delta$ values near 0‰, indicating total reduction of all available $SO_4^{--}$ in the system. Schwarz and Burnie believed that closed systems were to be found primarily in nearshore environments such as lagoons or estuaries where bodies of water isolated from free exchange with seawater can occur. This idea is sup-

Fig. 2

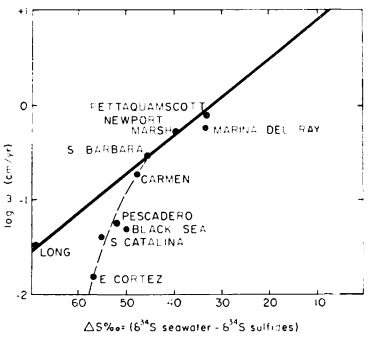


Fig. 3

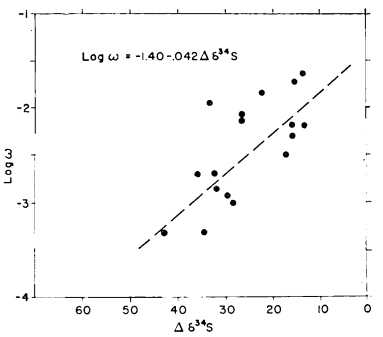


Fig. 2. Relationship between sedimentation rate and $\delta^{34}S$ in recent sediments. The line is from eq (4A). Data from Goldhaber and Kaplan (1975, figs. 3, 8) and Berner (1978, table 1).

Fig. 3. Relationship between sedimentation rate and $\delta\Delta^{34}S$ in Mesozoic shales of the Russian Platform and the Caucasus. From data of Ronov and others (1974, fig. 5 and table 4). $\Delta$ values calculated using the following values for seawater $\delta^{34}S$: Lias, + 17.2; Dogger, + 16.6; Early Cretaceous, + 15 (Nielsen, 1978, fig. 16-B-13). The line is drawn using the same slope as in figure 2 for comparison.

ported by data from Grinenko, Migdisov, and Barskaya (1973, table 1) who found increasingly negative $\delta^{34}S$ values going from brackish to marine environments in sedimentary rocks of the Russian Platform. Migdisov, Cherkovskiy, and Grinenko (1974) have also used this open versus closed basin model to explain sulfur isotopes in the Azov-Black Sea basin. They found a pronounced increase in $\delta\Delta^{34}S$ in going from the brackish waters of the Gulf of Taganrog ($\Delta \cong 20$) into the normal salinity waters of the Black Sea ($\Delta \cong 50$). Sedimentation rate may well parallel these changes in salinity, however, so that much of this variation may be due to decreasing $\omega$ rather than to a more open system.

Vinogradov, Grinenko, and Ustinov (1962, p. 984) have argued that if reduction occurs at some depth within the sediment rather than at the sediment-water interface, a closed-system model also applies. Goldhaber and Kaplan (1974, p. 632-643) have discussed this type of open-closed system behavior and have shown that closed-system sediments of the type hypothesized by Vinogradov, Grinenko, and Ustinov are characterized by low total sulfur content. Such behavior can, in fact, be seen in the sediments of the Black Sea (Vinogradov, Grinenko, and Ustinov, 1962). For the deep (2000 m) euxinic portion, pyrite sulfur averages 1.1 percent with $\delta^{34}S = -29.2‰$, while in the shallower (<200 m), oxygenated areas, sulfur is only about 0.2 percent and $\delta^{34}S = -16.7‰$ (p. 983-985). These sulfur concentrations support their contention that the sulfides in the oxygenated sediments have a more positive $\delta^{34}S$ because they were formed in a system closed to introduction of sulfate from the overlying water mass. However, sedimentation rate is also probably greater in these shallow water sediments, and thus control by rate of sedimentation rather than by the $SO_4^{--}$ supply cannot be ruled out. A comparative study of two areas of similar sedimentation rate but different degree of oxygenation of the surface sediment is needed.

Thus, we have essentially two different mechanisms by which sedimentary environment can affect sulfur isotopes of sulfides. First, there is the relationship between $\delta^{34}S$ and sulfate reduction rate, which is controlled by sedimentation rate. Then there is the degree of contact the sediment maintains with oceanic $SO_4^{--}$. If contact is poor, significantly less negative $\delta^{34}S$ (smaller $\Delta$) values are found. One way that such a closed system can occur is in a euxinic basin isolated from the open ocean, common in the early stage of evolution of an evaporite basin. Another possibility is in oxygenated sediments where sulfate reduction occurs too far below the sediment-water interface for free exchange with overlying seawater. This last type can be recognized by low total sulfur contents, around 0.1 to 0.3 percent. Naturally, there should be intermediate cases caused by incomplete exchange. Non-marine sediments would be a special case of an isolated basin.

## ANCIENT ROCKS: THE KUPFERSCHIEFER

As far as I am aware, the only previous extensive study of the sulfur isotopes of a single sedimentary unit in ancient rocks is Marowsky's (1969) work on the Kupferschiefer. This thin (<1 m), black, highly cal-

careous shale covers a large part of northwestern Europe and is enriched in Fe, Cu, Zn, and Pb sulfides. There are no apparent lateral changes in the sulfur isotopes, but most localities show a pronounced vertical trend in $\delta^{34}S$ of pyrite from an average of $-41‰$ at the base to $-27‰$ at the top. From the Permian seawater sulfate $\delta^{34}S$ of $+10‰$ (Holser and Kaplan, 1966, fig. 5), $\Delta$ is then 51 to 37‰. It seems unlikely that this change could reflect a change in sedimentation rate, because the vertical distances involved are so short — the sample spacing is in centimeters. Accordingly the relationship given by eq (4) probably does not apply. Schwarz and Burnie (1973, p. 268) inferred that this change was due to a progressively more closed sediment system. Marowsky (1969, p. 322), however, argues that the sulfur content is too high (1-5 percent) for the sediment to have been cut off from the overlying water. Instead, he suggests that the entire water body became progressively cut off from contact with open seawater, and thus the overlying water became correspondingly enriched in the heavier isotope (more positive $\delta^{34}S$) as the lighter $S^{32}$ was removed by bacterial sulfate reduction, leading to more positive $\delta^{34}S$ values in the later-formed sulfides. That is, $\Delta$ remained constant, but $\delta^{34}S$ of the sulfate in the seawater in the basin became more positive. The appearance of the evaporitic Zechstein sequence above the Kupferschiefer (Richter-Bernburg, 1955) favors this interpretation. If true, the other shaly units of the Zechstein, such as the Stinkschiefer or the Zechsteinletten, should also show cycles of $\delta^{34}S$ based on increasing and decreasing communication with the open ocean. Thus, such studies might be useful for interpreting paleocirculation patterns in evaporite basins.

The Kupferschiefer, then, is probably an example of an ancient black shale containing sulfide minerals whose isotopic composition is controlled by degree of contact of the basin of deposition with open seawater. How does this situation compare with the black shales of the Appalachian Basin?

## DEVONIAN-MISSISSIPPIAN ROCKS OF THE APPALACHIAN BASIN

Rocks of Devonian-Mississippian age in the western part of the Appalachian Basin consist of a thick clastic section made up of alternating black and gray shales with occasional turbidite siltstones (table 1). These coarser clastics become more abundant to the east and eventually pass into the non-marine clastics of the Catskill Delta (see for example, Colton, 1970). The turbidite siltstones are found almost exclusively in the gray shales, which in turn thicken sharply to the east. Thus, the gray shales are probably a proximal facies equivalent of the black shales deposited at higher sedimentation rates. The same facies interpretations were made years ago by Rich (1951). The units in the lower part of the section shown in table 1 are not well-developed in the study area (roughly the western half of the basin). In fact the entire section, from the top of the Sunbury Shale to the Middle Devonian limestones, shrinks from more than 2000 m along the Kentucky-West Virginia border to less than 15 m in south-central Kentucky and central Tennessee. The lower units drop out through an on-lap onto the Cincinnati arch, while the gray

TABLE 1

Stratigraphic units of the Devonian-Mississippian included in this study

| Name | Predominant Color | Lithology Mineralogy |
|---|---|---|
| Mississippian: | | |
| Borden Formation (= Price, Grainger) | Gray | Siltstone and shale. Turbidites abundant. Abundant siderite; marcasite near base in some areas. |
| Sunbury Shale | Black | Shale. Abundant pyrite. |
| Bedford Shale (+ Berea Sandstone) | Gray | Shale and siltstone with occasional siltstone turbidites (Euclid Member), Berea Sandstone irregularly present, mostly in Ohio. Bedford has siderite in base in Kentucky, large pyrite spheres (>2 cm) in top. |
| Devonian: | | |
| Ohio Shale | | |
| Cleveland Member | Black | Shale Pyritic |
| Chagrin Member | Gray | Shale and siltstone, turbidites common to east. Siderite abundant, pyrite common. |
| Upper Huron Member | Black | Shale Pyritic |
| Middle Huron Member | Gray and black | Shale, interbedded gray and black. Pyritic, occasionally some siderite. |
| Lower Huron Member (= Dunkirk of N.Y.) | Black | Shale Pyritic |
| Chattanooga Shale (= total Ohio Sh + Sunbury Sh where Bedford absent) | Black | Shale Pyritic, phosphate nodules abundant at top. |
| Java Group | | |
| Hanover Shale | Gray | Siltstone and Shale. |
| Pipe Creek Shale | Black | Thin black shale interbeds in gray shale. |
| West Falls Group | | |
| Angola Shale | Gray | Shale |
| Rhinestreet Shale | Predominantly black | Shale |
| Leicester Marcasite (becomes Tully Ls to east) | | Marcasite and pyrite replacing shell fragments |
| Unconformity | | |
| Hamilton group (undivided) | | (not studied) |
| Marcellus Shale | | |
| Unconformity | | |
| Middle Devonian and older carbonates | | |

shale units such as the Bedford and the Chagrin shales thin, so that the section becomes almost entirely black shale on top of the arch. Here it is referred to as the Chattanooga Shale (Wallace, Roen, and deWitt, 1977; Provo, Kepferle, and Potter, 1977).

The sulfur isotope distribution follows these lithologic variations (table 2), with those stratigraphic units that are inferred to have been more rapidly deposited having more positive $\delta^{34}S$ values. (Each number represents a single determination on a pyrite nodule.) In particular note that very positive values of $\delta^{34}S$ are found in pyrites from the Bedford Shale which was deposited in a rapidly prograding near-shore environment (Pepper, deWitt, and Demarest, 1954, p. 45-59) and is characterized by spherical pyrite nodules 1 to 2 cm in diameter. In contrast, relatively negative values of $\delta^{34}S$ are found in black shale units such as the Sunbury Shale and the Cleveland Member of the Ohio Shale, which contain flattened pyrite–marcasite nodules, often with large pyrite crystals on their upper surface, a texture that suggests slow direct precipitation from the water-column at the sediment-water interface (Goldhaber and Kaplan, 1974, p. 644). In particular, note the two very negative samples from Overton County, Tenn., near the crest of the Cincinnati arch, where the entire section, including the lower Mississippian, is compressed to less than 10 m and also the change in the Upper Part of the Huron Member of the Ohio Shale on going from the flank of the basin in Powell County, Ky. up on to the arch in Celina County, Tenn., the last outcrop in which subdivisions of the Ohio Shale are thick enough to be recognized. An anomalous occurrence is found in the turbidite siltstones of the Borden Formation, which are very negative compared with other gray shale–siltstone units in the section. I have argued elsewhere (Maynard and Lauffenburger, 1978) that these sulfides, which are largely marcasite, formed slowly, after the deposition of the overlying beds. The textures of the other pyrites, however, particularly the spherical ones, suggest early formation of the nodules, before appreciable compaction.

Although there is qualitative agreement between these results and a simple sedimentation rate control of $\delta^{34}S$, quantitative agreement is poor. Most of the values are too positive by about 10 to 20‰ for rea-

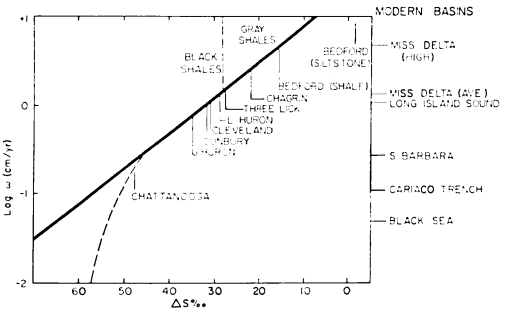


Fig. 4. $\delta^{34}S$ values from Devonian-Mississippian shales compared with the sedimentation rate curve from recent sediments. Note the unrealistically high sedimentation rates that result.

TABLE 2

Sulfur isotopic composition of iron sulfides from Devonian-Mississippian rocks of the Appalachian Basin. Each value is from a single determination.

| Stratigraphic unit | Mineralogy (from polished sections) | $\delta^{34}S$ |
|---|---|---|
| 1. Borden Formation | | |
| Farmer's Siltstone Member | | |
| (Rowan Co., Ky.) | marcasite | −11.1 |
| (Rowan Co., Ky.) | marcasite | −21.4 |
| Kenwood Siltstone Member | | |
| (Bullit Co., Ky.) | pyrite | −11.1 |
| 2. Sunbury Shale | | |
| (Adams Co., Ohio) | | − 7.4 |
| (Rowan Co., Ky.) | pyrite | − 5.9 |
| 3. Bedford Shale | | |
| (Rowan Co., Ky.) | | +20.0 |
| (Rowan Co., Ky.) | pyrite | +16.6 |
| (Cuyahoga Co., Ohio) | pyrite | − 7.5 |
| Euclid Siltstone Member | | |
| 1 m turbidite bed | | |
| (Cuyahoga Co., Ohio) | | +26.7 |
| 4. Ohio Shale | | |
| Cleveland Member | | |
| (Cuyahoga Co., Ohio) | | − 9.2 |
| (Lorain Co., Ohio) | | − 5.2 |
| (Rowan Co., Ky.) | | − 3.6 |
| (Powell Co., Ky.) | | − 4.6 |
| (Adams Co., Ohio) | | − 6.7 |
| Chagrin Member | | |
| (Lorain Co., Ohio) | | + 2.6 |
| (Wise Co., Va. — core) | | + 3.3 |
| Three Lick Bed of Chagrin | | |
| (Rowan Co., Ky.) duplicate proportion | | −2.6, − 3.2 |
| Upper Huron Member | | |
| (Powell Co., Ky.) | | −10.1 |
| (Celina Co., Tenn.) | | −19.5 |
| Middle Huron Member | | |
| (Adams Co., Ohio) | Pyrite + calcite | +23.5 |
| (Powell Co., Ky.) | | −10.8 |
| (Wise Co., Va. — core) | | +29.8 |
| *Foerstia* zone of Middle Huron | | |
| (Duffield, Va.) | | + 1.9 |
| (Adams Co., Ohio) | | − 0.6 |
| (Powell Co., Ky.) | | + 0.4 |
| Lower Huron Member | | |
| (Wise Co., Va. — core) | | − 3.8 |
| (Wise Co., Va. — core) | | − 6.5 |
| (Wise Co., Va. — core) | | − 7.1 |
| (Delaware Co., Ohio — core) | pyrite + calcite | + 6.3 |
| (Delaware Co., Ohio — core) | pyrite | − 0.9 |
| (Rowan Co., Ky.) | marcasite + pyrite | − 8.7 |
| (Rowan Co., Ky.) | marcasite + pyrite | − 3.6 |
| Chattanooga Shale | | |
| (Overton Co., Tenn. — core) | | −20.5 |
| (Overton Co., Tenn. — core) | | −29.9 |
| (Giles Co., Tenn.) | | −18.3 |
| Unconformity at base of Ohio Shale | | |
| (Adams Co., Ohio) | | |
| massive pyrite | | − 4.2 |
| sandy, phosphatic zone | | −24.2 |
| (Rowan Co., Ohio) | | |
| sandy, phosphatic zone | marcasite + pyrite | −29.0 |
| 5. Leceister Marcasite — massive sulfide | | |
| (Erie Co., N.Y.) | | |
| top | | − 1.4 |
| base | | − 0.2 |
| Averages | | |
| Unconformities | | −11.8 |
| Black shales | | − 8.9 |
| Gray shales | | +11.6 |
| Later mineralization (Borden) | | −14.5 |

sonable sedimentation rates (fig. 4), if we use the accepted average value of +25‰ for Upper Devonian seawater sulfate (Holser and Kaplan, 1966, fig. 5) to calculate Δ values. Note, for instance, that the middle part of the Huron Member of the Ohio Shale and the Bedford Shale would have been deposited at rates significantly higher than average nearshore sediments of the Mississippi delta, which is most unlikely. That is, the implied sedimentation rates seem to be too high by a factor of about 5, if we assume that the Bedford Shale was deposited at about 1 cm/yr, which seems to be the maximum for normal nearshore marine sediments (Berner, 1978, table 1). Also the black shales of the Cleveland and Lower Huron would then have been deposited at about the same rate as the sediments of the Santa Barbara Basin.

How can this discrepancy be accounted for? There are several possibilities. First, it is conceivable that the biochemistry of the sulfate reduction process was different in the Devonian. This possibility can only be tested by examining sedimentary sulfides in several depositional basins over the whole Phanerozoic. There is, however, no reason to suppose that the Devonian bacteria were any different from modern ones. Therefore, this explanation should be set aside until some independent evidence for it appears. It is more likely that our data from the recent is inadequate. The equations used may be biased by a few unrepresentative samples, or there may be some unsuspected diagenetic change in $\delta^{34}S$. For instance, many of the sulfides used in figure 1 are actually FeS rather than pyrite. In all likelihood, the pyrite in the Devonian shales is secondary after early FeS. Could the transition to the more stable form, $FeS_2$, lead to more positive $\delta^{34}S$ values? Results from most workers (Vinogradov, Grinenko, and Ustinov, 1962; Goldhaber and Kaplan, 1974, 1975) suggest there is no appreciable change in $\delta^{34}S$ in the progression $H_2S \rightarrow FeS \rightarrow FeS_2$. However, it was decided to test the possibility that later-formed sulfides in these rocks might have more positive $\delta^{34}S$. Accordingly, a 3 cm thick pyrite nodule from the Cleveland Member of the Ohio Shale in Rowan County, Ky. was analyzed serially for $\delta^{34}S$. The nodule consisted of a microcrystalline core, about 1 cm thick, with what appear to be shrinkage cracks, followed by a macrocrystalline layer, again about 1 cm thick, followed by a thin coating of radiating, fibrous crystals (fig. 5). The $\delta^{34}S$ values for each layer are almost identical, showing that no change

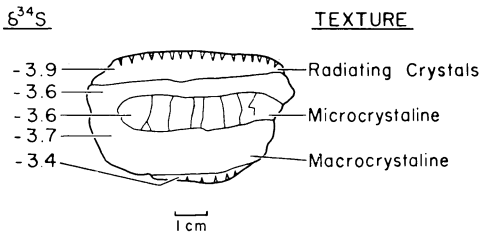


Fig. 5. Distribution of $\delta^{34}S$ within a pyrite nodule from the Cleveland Shale, showing no change during growth of the nodule.

occurred during the formation of the nodule, although it is still conceivable that the entire nodule formed from heavy $SO_4^{--}$ late in the diagenetic history of the sediment.

An additional methodological problem is that all of the values reported in table 2 are from sizeable nodules, most larger than 1 cm in diameter. The modern sediment samples, on the other hand, contained mostly very fine grained sulfides. Could it be that there is a difference in $\delta^{34}S$ among various sizes of pyrite? If nodules form very late in the history of the sediment, they should be isotopically much heavier than the early-formed sulfides (Goldhaber and Kaplan, 1974, p. 638-639). However, most sulfide formation seems to be near the sediment-water interface, so that late sulfides are not likely to be quantitatively important. For instance, Goldhaber and Kaplan (1974, tables 25 and 27) present data that show no difference in $\delta^{34}S$ over the size range 104 to 44 $\mu$m. In some cases the coarser grained pyrite was actually more negative, suggesting that the smaller sulfide grains are the late-forming ones. As part of a study of the organic matter in the Devonian shales, we performed several kerogen isolations. In this process, all the mineral matter is dissolved except for pyrite. A study of silt-sized (62.5-3.9 $\mu$m) pyrites from these isolates gave results entirely consistent with those from the nodules. However, the pyrite intimately mixed with the kerogen gave values consistently more negative by 20‰. Examination of thin sections of the shale shows abundant pyrite-filled spores, often uncompressed. These are probably important contributors to this "organic-bound" pyrite. I have no explanation for the difference in $\delta^{34}S$, but it does illustrate that care must be taken to work with the same types of samples in any study such as this. In particular, data from nodules are likely to differ from whole-rock analyses. It is possible, even likely, that data from these "matrix" sulfides is in fact more closely comparable to modern sediments. Certainly the difference in $\delta^{34}S$ is in the right direction. If so, we have much to learn about the geochemistry of diagenesis of sulfides. The two types of sulfides seem to be self-consistent, however, and the nodules are easier to work with, especially in outcrop.

An additional observation suggests that the nature of the sample is very important. Pyrite associated with coarsely crystalline calcite seems to be about 5‰ heavier than normal pyrite. Of the two samples from the Lower Huron in Delaware County, Ohio (table 2) the one with $\delta^{34}S = +6.3$ had such calcite intergrown with it. Note this value is distinctly different from the nearby sample, which had no calcite, and from other samples from this stratigraphic unit. There is, at the base of the Lower Huron in Ohio, a zone of very large calcite concretions. Pyrite associated with these concretions also showed very heavy $\delta^{34}S$ values, as high as +14. Apparently, the processes leading to the formation of sulfides associated with these diagenetic carbonates differ from those forming the other pyrite nodules. However, this is the only evidence from these rocks so far of heavier pyrite caused by diagenesis.

Let us consider some other explanations. Could these rocks have behaved as closed systems? We can dismiss the idea that the sediments themselves acted as a system closed to overlying seawater, as they seem to be for the oxygenated parts of the Black Sea, because sulfur contents are uniformly high: about 1.9 percent for gray shales and 2.8 percent for black shales in Perry County, Ky. (M. Vickers, personal commun., 1976). However, the pyrite from the turbidite bed in the Euclid member of the Bedford may well have obtained its very positive (+26.7) value in this way. Accordingly, this sample was not included in the average for the Bedford Shale. There is, however, the possibility that, like the Kupferschiefer, the Appalachian Basin was somewhat isolated from normal seawater during the Upper Devonian-Lower Mississippian, and $\delta^{34}S$ became very positive by preferential removal of $S^{32}$ by sulfide formation. If so, the $\delta^{34}S$ of water in the basin must have been about +35‰ and stayed near that value during the entire period these rocks were deposited. Holser and Kaplan (1966, fig. 7) show that evaporites in the Upper Devonian of western North America had widely fluctuating $\delta^{34}S$ values, as high as +34‰, but falling to +20‰ in the Mississippian. Therefore, a stable system with strongly positive $\delta^{34}S$ values seems unlikely for the Devonian of the Appalachian Basin. Also, unlike the Kupferschiefer, these rocks are not immediately overlain by large evaporite deposits, nor is there any faunal evidence for unusual salinity.

Despite these uncertainties about the absolute relationship of $\delta^{34}S$ to rate of sedimentation, it is possible if care is taken to use the same types of samples in the comparison, to construct a relative sedimentation rate scale for the Devonian-Mississippian (table 3). It is important to remember that the scale is only a relative one and is based on two unconfirmed assumptions: that $\delta^{34}S$ of seawater sulfate was nearly constant throughout the basin, and that it did not change appreciably during the deposition of these rocks.

Such a sedimentation rate scale should have a number of applications in the study of shales. For instance, preliminary work in our laboratory suggests that trace element concentrations are in part controlled by sedimentation rate. Another area of application is to the study of the organic matter in shales. Table 3 shows that there was about a two-fold

TABLE 3

Relative sedimentation rates inferred from sulfur isotopes

| Stratigraphic unit | Number of samples | Relative sedimentation rate* |
|---|---|---|
| Bedford Shale | 3 | 1.0 |
| Chagrin Shale | 2 | 0.5 |
| Three Lick Bed | 1 | 0.3 |
| Foerstia Zone of Middle Huron | 3 | 0.4 |
| Lower Huron Member of Ohio Shale | 5 | 0.3 |
| Cleveland Member of Ohio Shale | 4 | 0.2 |
| Sunbury Shale | 1 | 0.2 |
| Upper Huron Member of Ohio Shale | 1 | 0.15 |
| Chattanooga Shale | 2 | 0.04 |

* Based on assigning the Bedford a rate of 1 in arbitrary units.

difference in sedimentation rate between the gray and the black shales in this basin. Is this difference enough to account for the difference in organic content, or is an additional factor responsible? That is, is the rate of sedimentation the only important variable? If we regard the inorganic material as simply diluting a constant supply of organic matter, then the resulting carbon content of the rock is given by

$$\text{percent C} = O/(O + S)$$

where O is the *net* flux of organic matter and S is the flux of mineral matter in mg/cm$^2$ • yr. The rate of sedimentation, $\omega$, is related to these variables by the bulk density:

$$O + S = \omega\rho.$$

Combining

$$\omega = \rho O/\text{percent C}.$$

If O is constant, a plot of $\omega$ versus $1/\%C$ should be a straight line. The Devonian-Mississippian rocks show instead two distinct lines, one for black and one for gray shales (fig. 6). I suggest this is due to a higher value for O during the time the black shales were being deposited caused by a slower rate of organic matter decay, in turn caused by lower oxygen content in the bottom water. Such an interpretation is consistent with the difference in pyrite morphology between the two shale types and with the trace fossil differences reported by Cluff (1978) and Byers (1977).

## CONCLUSIONS

Studies from recent sediments show that the sulfur isotopic composition of sulfide minerals is controlled ultimately by the sedimentation rate, although initially by the rate of sulfate reduction, which increases with increasing sedimentation rate. This primary effect is then modified by the degree of contact with open seawater. If contact is restricted, the resulting $\delta^{34}S$ values are more positive. Such restriction can result from a restricted basin or possibly from sulfide formation well below (>10 cm) the sediment water interface in a relatively well-oxygenated basin. These

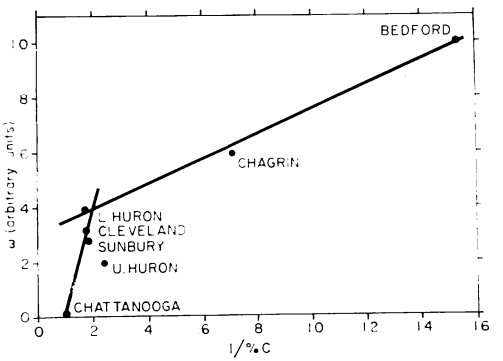


Fig. 6. Relationship between organic carbon content and sedimentation rate. The two distinct curves for black and gray shales suggest that sedimentation rate alone does not account for the difference in organic content; some other factor such as oxygenation of the bottom water must be important.

two types are easily distinguished by low sulfur contents (<0.3 percent) in the second case.

Similar patterns are seen in ancient shales. Sulfur isotope results from the Kupferschiefer suggest an initially open basin followed by increasingly restricted conditions, culminating in the Zechstein evaporite sequence.

Devonian-Mississippian shales of the western part of the Appalachian Basin show more positive $\delta^{34}S$ values of pyrite in the proximal gray shales, more negative in the distal black shales. Extremely negative values are found in the very thin black shales along the crest of the Cincinnati arch. These results strongly suggest control of $\delta^{34}S$ in these rocks by sedimentation rate. Comparison with the sedimentation-rate curve from recent sediments, however, gives rates much too high. Four explanations for this discrepancy come to mind:

1. The biochemistry of sulfate reduction has changed since the Devonian.
2. The recent sediment curves are not quantitatively adequate because of too few data points.
3. There is a change in sulfur isotopic composition on going from the fine-grained FeS of recent sediments to the coarse $FeS_2$ of the nodules in the ancient rocks.
4. The basin of deposition of the Devonian-Mississippian shales was sufficiently restricted from contact with the open ocean to build up a large reservoir of heavy sulfur.

Some younger rocks such as the Pierre Shale or the Mowry Shale need to be studied to test (1). For (2) and (3), more data are needed from recent sediments from basins where both $\delta^{34}S$ and sedimentation rate data are available. Perhaps (4) can be answered by studying the Appalachian Basin more thoroughly.

As mentioned, (1) is an unattractive hypothesis, if only because of the simplicity rule. (4) requires an unlikely combination of circumstances. Thus, (2) and (3) seem at this time to be most likely.

Whatever the cause of the quantitative discrepancy, the data from the pyrite nodules for the Devonian shales is internally consistent with the sedimentation-rate model for the composition of sulfur isotopes. Accordingly, I believe that such measurements can be used to infer relative sedimentation rates in ancient rocks. Care must be used, however, to insure that similar types of samples are being compared.

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