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Sulphate reduction, organic matter decomposition and pyrite formation

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Laboratory, field, and theoretical studies have shown that the rate of bacterial sulphate reduction during early diagenesis depends primarily on the reactivity of sedimentary organic matter whose decomposition follows first-order kinetics, with rate constants varying over six orders of magnitude. Decay rates decrease with decreasing sediment burial rate and, for a given sediment, with depth, because of the successive utilization by bacteria of less and less reactive organic compounds. High burial (and bioturbation) rates enable reactive compounds to become available for sulphate reduction, at depth, which otherwise would be destroyed by molecular oxygen at or above the sediment–water interface.

An important consequence of bacterial sulphate reduction is the formation of sedimentary pyrite, FeS_2. In normal marine sediments (those deposited in oxygenated bottom waters) pyrite formation is limited by the concentration and reactivity of organic matter, whereas in euxinic (sulphidic) basins pyrite is limited by the abundance and reactivity of detrital iron minerals, and in non-saline swamp and lake sediments by the low levels of dissolved sulphate found in fresh water. Because of these differences in limiting factors, the three environments can be distinguished in both modern sediments and ancient rocks by plots of organic carbon, C against pyrite sulphur, S. Values of the C:S ratio based on theoretical calculations indicate that worldwide the bulk of organic matter burial has shifted considerably between these environments over Phanerozoic time.

1. Introduction

The vast bulk of the world's sediment carried by rivers to the oceans is deposited now and was also deposited in the geologic past along the continental margins. It is here also where most of the world's organic matter is deposited, some of this being derived from terrestrial plant debris delivered by the rivers and some produced by marine organisms. Because an overriding theme of this symposium is the diagenesis of organic matter, it is instructive to examine what happens when this matter first becomes buried in continental margin sediments. The emphasis in this paper will be on the processes accompanying organic matter decomposition during shallow burial in typical marine muds or, in other words, on early diagenesis.

It is generally not realized that over 90% of all medium- to fine-grained sediments buried in the marine environment become anoxic below the top few centimetres (see, for example, Berner 1982). Anoxicity arises from the total consumption of dissolved oxygen by bacteria and other micro-organisms living near the sediment–water interface that prevent the further migration of O_2 to deeper levels in the sediment. As a result, continued organic matter decomposition at depth takes place only by anoxic processes, and the principal process in continental margin sediments is bacterial sulphate reduction. The strictly anoxic community of sulphate-reducing bacteria, consisting of the sulphate reducers themselves and associated fermentatative micro-organisms, obtains energy by oxidizing organic matter to CO_2 while reducing dissolved interstitial sulphate to H_2S. Overall the reaction can be written as

$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-. \tag{1}$$

The hydrogen sulphide produced by this reaction either migrates upward (or laterally where shallow worm burrows are present (Aller 1980)) to oxygenated portions of the sediment where it is oxidized back to sulphate or reacts with detrital iron minerals in the sediment to form various iron sulphides, with the chief end product being pyrite, FeS_2. (This is shown in figure 1.) Thus, the overall process of organic matter decomposition in continental margin sediments is inextricably intertwined with the additional processes of both sulphate reduction and pyrite formation. This association is important because, as will be seen, it can be used to deduce the environment of deposition of organic matter in ancient sediments and how the relative importance of each environment has changed over geologic time.

Organic decomposition, sulphate reduction and pyrite formation can also take place in sediments other than those typical of the continental margin. Practically all continental margin sediments (as well as deep-sea sediments) are deposited in oxygenated bottom waters. (It is only at depth in the sediment that anoxic conditions, necessary for sulphate reduction, are attained.) By contrast, at a few scattered localities deposition occurs in bottom waters that contain dissolved H_2S and no oxygen. Such environments are termed 'euxinic', with the type example being the deeper water portions of the Black Sea (from whence the term euxinic is derived, the ancient Latin name for the Black Sea being Pontus Euxinus). Euxinic environments arise from tectonic, physiographic, climatic and oceanic factors that bring about the isolation of stagnant deep water bodies from contact with atmospheric oxygen and thus allow the build-up of H_2S. At almost all other places in the modern ocean, because of the presence of O_2, build-up of H_2S cannot occur and the term 'normal marine' is applied to these sediments to distinguish them from the much rarer euxinic ones.

Organic matter decomposition, accompanied by sulphate reduction and pyrite formation, also occurs on land in swamp and lake sediments. Here, however, the dominant process of anoxic organic matter decomposition is methane formation, not sulphate reduction (see, for example, Reeburgh & Heggie 1977). Because of low concentrations of dissolved sulphate in fresh water (in contrast to the much higher level in sea water), total sulphate removal is complete near the sediment–water interface and continued organic decomposition at depth is accomplished by the breakdown of organic matter to methane and carbon dioxide without the production of appreciable H_2S.

Organic matter decomposition and burial in the environments of normal marine, euxinic, and non-marine freshwater, results in differences at depth in the concentrations of organic carbon (C) and pyrite sulphur (S), which can be used to distinguish the three environments in ancient sedimentary rocks (Leventhal 1983*b*; Berner & Raiswell 1984). In addition, observed C:S relations in modern sediments can be used to explain why the worldwide average C:S ratio for all sediments has varied over geologic time (Berner & Raiswell 1983; Arthur 1983). Thus, studies of modern continental margin sediments, besides being interesting in their own right, can be used to get at several problems concerning the burial of organic matter and reduced sulphur over geologic time. As we will see, the relative importance of the three environments has varied considerably over the past 600 Ma.

2. Modern sediment studies

An important process that can be used to distinguish environments of organic matter deposition is pyrite formation. The overall process of sedimentary pyrite formation, as discussed above, is summarized in figure 1. (For further discussion consult the reviews by Goldhaber & Kaplan (1974), Curtis (1977) or Berner (1984).) As can be seen, the three principal factors that ultimately limit how much pyrite may form are (i) the amount and reactivity toward sulphate reduction of organic matter supplied to the sediments; (ii) the amount and reactivity toward H_2S of detrital iron minerals supplied to the sediment and (iii) the availability of dissolved sulphate. In § 2 the formation of pyrite and the ways in which these factors limit pyrite formation in each of the normal marine, euxinic, and freshwater environments are documented.

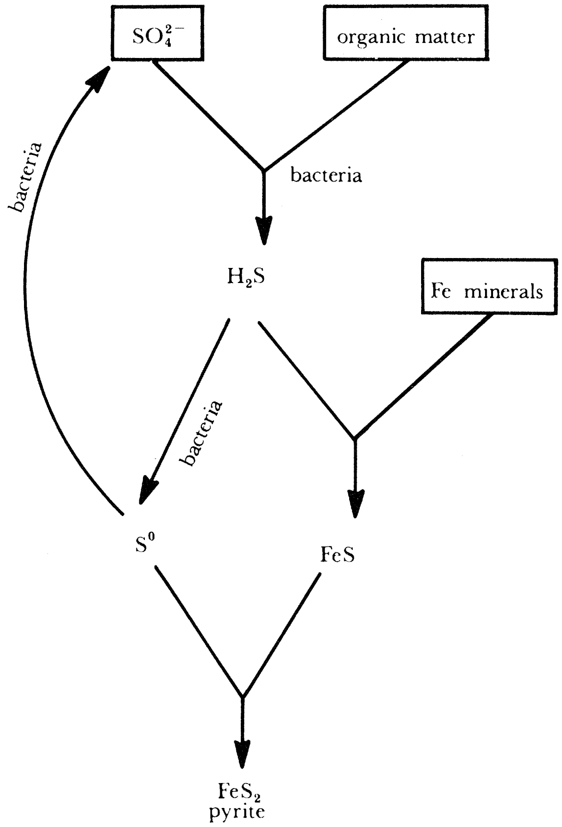

Figure 1. Schematic diagram summarizing the major steps in sedimentary pyrite formation. (After Berner 1972.)

(a) *Organic matter: normal marine environments*

The first step in sedimentary pyrite formation is bacterial sulphate reduction. From figure 1 and (1) it might be expected that the rate of sulphate reduction in sediments is controlled by the availability of organic matter or sulphate or both. Recent work (Westrich 1983; Westrich & Berner 1984; Boudreau & Westrich 1985) has conclusively shown that, in marine sediments, the dominant control is by organic matter availability and not sulphate. Also, organic matter exerts its influence in terms of its reactivity rather than its total concentration.

Theoretical studies (see, for example, Berner 1980) and rate measurements with the use of ^{35}S (Westrich 1983) have shown that organic matter in surficial sediments can be divided into a number of groups depending on the reactivity of each group toward sulphate reduction. In addition, both theoretical and experimental studies (Westrich & Berner 1984) have shown that the rate of decomposition via sulphate reduction of each group is directly proportional to its concentration. Mathematically this can be expressed as

$$\frac{dG_i}{dt} = -k_i G_i, \tag{2}$$

$$G_t = \sum_{i=1}^{n} G_i, \tag{3}$$

$$\frac{dG_t}{dt} = -\sum_{i=1}^{n} k_i G_i, \tag{4}$$

where G_i is the concentration of organic carbon in reactivity group i, k_i is the first-order rate constant and G_t is the total organic carbon in the sediment. Here, G_i represents the amount of each group and k_i its reactivity.

Demonstration of both the importance of organic matter and the validity of (2) is shown in figure 2. This figure shows that the addition of organic matter to an organic-depleted sediment stimulates sulphate reduction at a rate directly proportional to the amount of carbon added. (The slope of each line is equal to k_i in (2).) The figure also shows that for aged organic matter, present here as oxically degraded plankton remains, the rate constant k is lower than

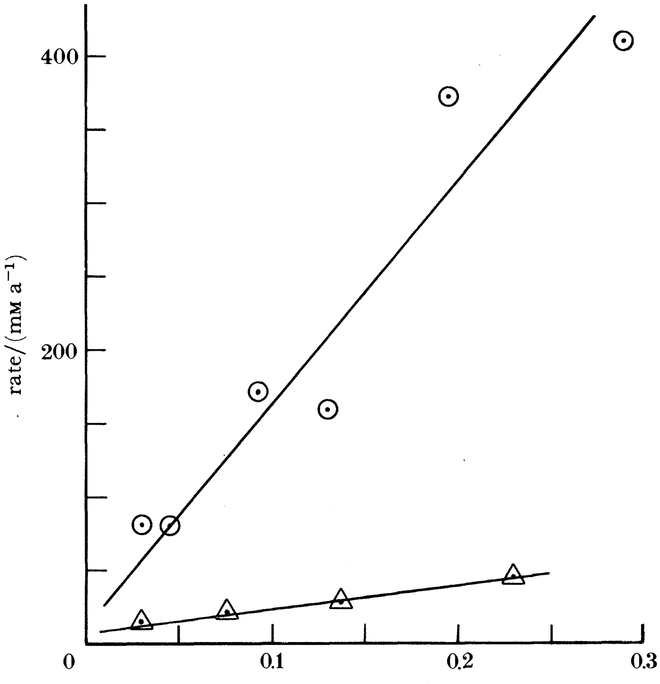

FIGURE 2. Results of 'feeding' experiments where fresh plankton (⊙) and plankton degraded oxically for 72 days (△) were each added to Long Island Sound sediment samples in varying amounts. Rate refers to rate of sulphate reduction as determined by using a ^{35}S tracer. Data from Westrich & Berner (1984). (See also Berner 1984.)

that for fresh organic matter. Similar results are found for anoxically degraded sediment organics. Apparently, during diagenesis the reactivity of organic matter toward bacterial sulphate reduction progressively decreases as the more rapidly metabolizable compounds are consumed or as more resistant geopolymers are formed. This leads to a decrease in k_i and consequently R_i, the rate of sulphate reduction of each group, with depth (see, for example, Jorgensen 1978). An example taken from sediments of Long Island Sound is shown in figure 3. Note that the drop in rate cannot be a result of dissolved sulphate, the concentration of which remains essentially constant with depth.

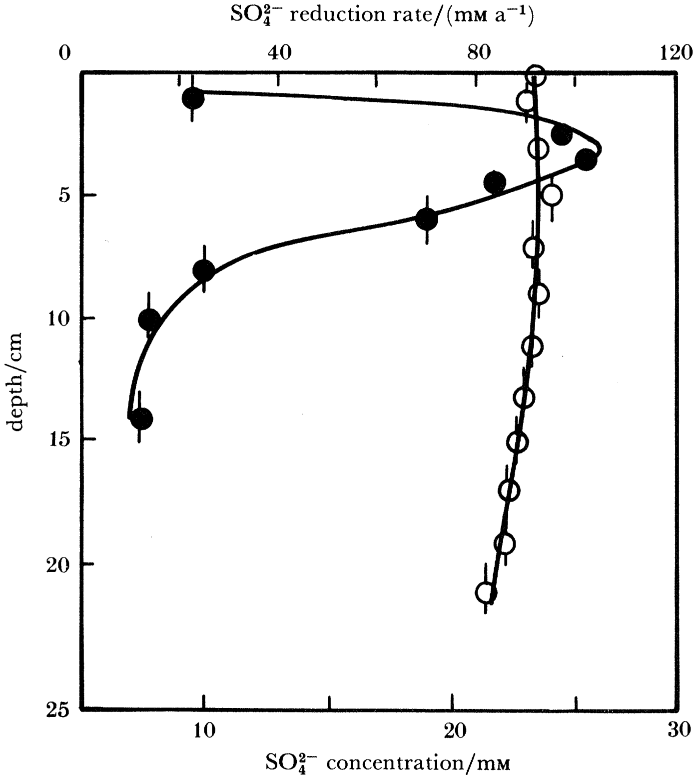

FIGURE 3. Plots of sulphate reduction rate by using a ^{35}S tracer (●) and concentration of dissolved sulphate (○) against depth in a sediment (FOAM site) from Long Island Sound. (The low value for reduction rate in the top 2 cm is because of constant reoxygenation of large proportions of sediment within this depth range by burrowing infauna). Data from Westrich (1983).

Besides decreasing with depth, average values of k also decrease from one locality to another as the rate of sedimentation decreases. In slowly deposited sediments there is sufficient time for the destruction of reactive (high k) organic compounds at the sediment–water interface by oxic organisms before the compounds can become buried and made available to the sulphate-reducing community. Thus, the residual organic matter that is buried, besides being less abundant, is also less reactive. Conversely, in rapidly deposited sediments, more organic matter and more reactive compounds are buried to anoxic depths before they can be oxically destroyed and as a result sulphate reduction rates are higher. (Burial of organic matter is also enhanced by burrowing benthic organisms that rapidly inject fresh organic compounds at depth, which ultimately become available for sulphate reduction.) This all leads to a good positive correlation between the average k at each site and the rate of sedimentation (Toth & Lerman 1977; Berner 1980). Compilation of k values, based on rate measurements and diagenetic modelling (Westrich 1983), indicate a large total worldwide range in k of more than a million-fold, reflecting the large worldwide range in sedimentation rate.

In normal marine sediments, except for those consisting almost entirely of biogenic silica or calcium carbonate, there is sufficient detrital iron present to ensure that pyrite formation is not limited by iron. (This is demonstrated by the presence of excess iron at depth in these sediments after all the pyrite has formed.) Thus, the limiting factor in normal marine pyrite formation must be involved in bacterial sulphate reduction and, as shown above, this means organic matter. Higher rates of H_2S production, by organically controlled sulphate reduction, allows a greater proportion of the iron minerals present to be transformed to pyrite. The iron minerals normally react slowly with H_2S, and because of this slowness, most of the H_2S escapes from the sediment before it can react with the iron minerals. This is shown in table 1. In addition, iron sulphides are oxidatively destroyed by O_2, which is mixed into the sediment by the burrowing activities of benthic organisms (see, for example, Aller 1980). This means that much additional organic matter, especially reactive organic matter, is needed to maintain levels of H_2S to resupply that lost from the sediment and to reconvert oxidized iron minerals back to pyrite. In other words, the amount of organic carbon needed to support sulphate reduction is much greater than that recorded by the amount of pyrite buried (see table 1).

TABLE 1. CALCULATED AGAINST MEASURED REDUCED SULPHUR, FORMED OVER THE DEPTH RANGES INDICATED, FOR LONG ISLAND SOUND SEDIMENTS[a]

location (depth/cm)	percentage S calculated	percentage S measured	percentage H_2S buried as pyrite
FOAM (0–100)	6.96	1.08	15
NWC (0–150)	18.70	1.05	6
Sachem (0–50)	2.40	1.14	47
BH (0–10)	3.39	0.96	28

[a] Calculated values represent total H_2S formed by bacterial sulphate reduction as determined by integrating measured ($^{35}SO_4$) reduction rates over each depth range. Measured values represent H_2S that was actually precipitated and buried as pyrite. (The FOAM and NWC locations are more typical of normal marine sediments in general). Data from Westrich (1983).

The above arguments suggest that a good positive correlation between pyrite sulphur and residual organic carbon (as a measure of that originally supplied to the sediment) should be exhibited by normal marine sediments. This is actually found to be so. Figure 4 shows that such a correlation exists, based on hundreds of chemical analyses of modern sediments from all over the world. Thus, the primary factor limiting pyrite formation in normal marine sediments, i.e. those deposited in oxygenated bottom waters, is organic matter and the normal marine environment should thus be distinguishable by a positive correlation between organic carbon and pyrite sulphur with zero intercepts for both.

(*b*) *Detrital iron minerals: euxinic environments*

A major difference between euxinic and normal marine environments is that in euxinic environments pyrite can form at locations where no organic matter is deposited. This is because H_2S is present everywhere in the bottom waters. An iron mineral falling to the bottom of a

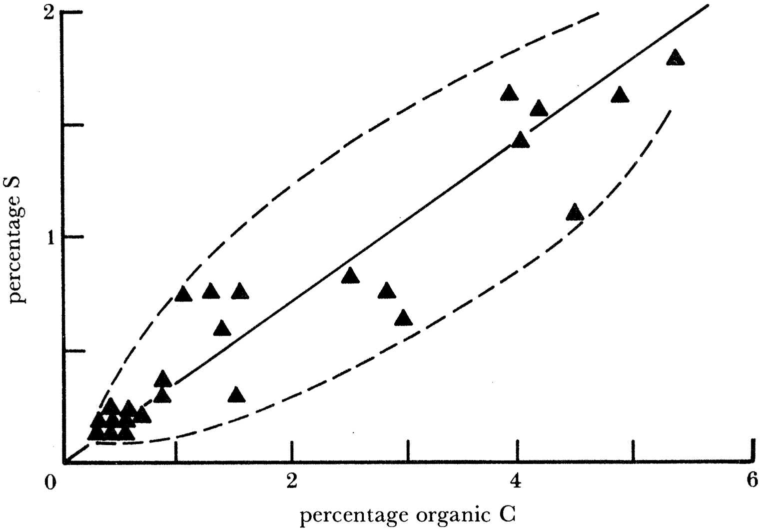

FIGURE 4. Plot of pyrite sulphur (S) in percentage by mass against percentage of organic carbon (C) for modern normal marine sediments. Plotted points represent preferred values; broken lines enclose hundreds of additional analyses as summarized by Leventhal (1983*a*) from the compilation of Sweeney (1972) and Goldhaber & Kaplan (1974). After Berner & Raiswell (1983).

euxinic basin at any given location can react with H_2S even though there is no organic matter present. Of course, basinwide, organic matter is required to produce H_2S via bacterial sulphate reduction, but this can occur elsewhere, even in the overlying water (Sweeney & Kaplan 1980). Lateral advection supplies H_2S to the deep waters and consequently smoothes out possible concentration differences resulting from lateral differences in production rate.

Besides lateral advection, H_2S abundance in euxinic basins is also a result of the nature of organic matter sedimenting to the bottom. Under normal marine conditions much of the most reactive organic compounds are destroyed by oxic decomposition in the overlying oxygenated water column before they can be buried and become available for sulphate reduction. By contrast, in euxinic basins organic matter falling toward the bottom is rapidly introduced to anoxic, sulphidic waters before appreciable oxic decomposition can take place. As a result more reactive organic compounds become available for bacterial sulphate reduction both in the deeper portions of the water column and on the bottom. This leads to a greater proportion of H_2S for each C atom sedimenting to the bottom than occurs in normal marine environments.

Because of the abundance of H_2S, pyrite formation in euxinic basins should be limited by the amount and reactivity of iron minerals. This is actually found to be the case, for example, for the deep-water sediments of the Black Sea (Ostroumov *et al.* 1961). By contrast, a good correlation between pyrite sulphur (S) and organic carbon (C) is generally not found. This is shown for Black Sea sediments in figure 5. Poor C–S correlation occurs because appreciable pyrite can form at low concentrations of organic carbon as explained above. In fact the presence at low carbon on C–S plots of points well above the normal marine regression line provides a ready way of distinguishing euxinic from normal marine sediments, a finding already advanced by Leventhal (1983*a*).

One might think that all detrital iron falling to the bottom of euxinic basins is converted to iron sulphide. This is not normally the case (see, for example, Berner 1984). Because of very slow reaction, some iron minerals such as silt-sized grains of hornblende and augite escape being

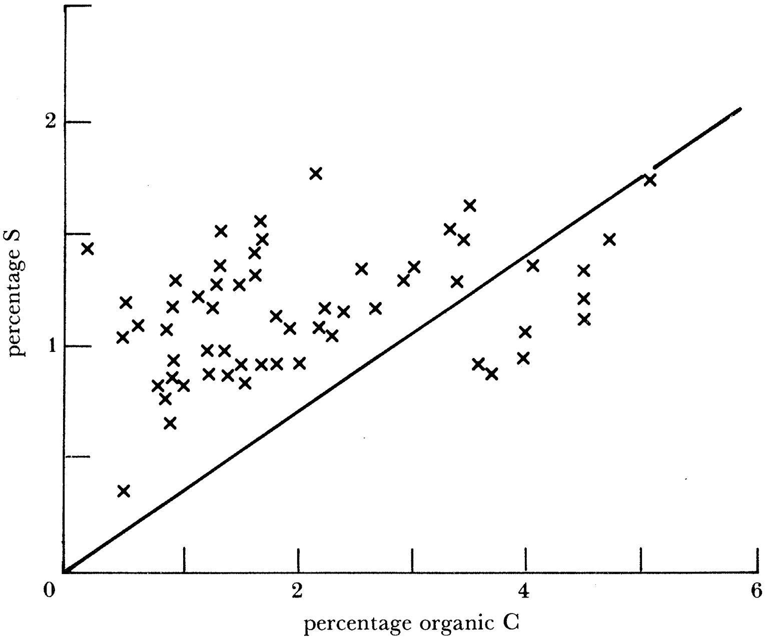

FIGURE 5. Plot of pyrite sulphur against organic carbon for euxinic, deep-water sediments of the Black Sea. Data from Rozanov *et al.* (1974). The straight line is the regression line for normal marine sediments taken from figure 4. After Berner (1984).

converted entirely to pyrite. Only the more reactive phases, especially fine-grained hydrous iron oxides present as rusty coatings on detrital grains, are sulphidized. This results in appreciable quantities of excess iron buried in euxinic sediments that have not been converted to pyrite (see, for example, Rozanov *et al.* 1974). It also results in the excess iron found in normal marine sediments as described earlier. Consequently, the positive correlation found between sulphur and iron, in both modern and ancient euxinic sediments, does not usually extrapolate to zero iron at zero pyrite; there is an excess, unreactive fraction present. Occasionally ancient euxinic shales are found where all the iron has been converted to pyrite (J. Leventhal, personal communication), but in such cases either the source of iron must have been limited to unusually reactive minerals, or depositional burial was so slow, or both, so that the iron minerals were subjected to prolonged reaction with H_2S over exceedingly long periods.

(*c*) *Dissolved sulphate: freshwater environments*

In contrast to the normal marine environment, sediments deposited in fresh water are depleted in dissolved sulphate. This occurs because the sulphate concentration in most fresh waters is hundreds of times lower than that found in sea water. Consequently, pyrite formation in freshwater lake and swamp sediments is limited by dissolved sulphate. During the initial stages of organic matter decomposition sulphate rapidly becomes exhausted and pore waters of swamp and lake sediments are characterized by a lack of sulphate below the top few centimetres (see, for example, Emerson 1976). The small amount of H_2S formed is rapidly precipitated as FeS and pyrite and subsequent diagenesis results not in the formation of additional H_2S but in the liberation of iron to solution. Some extra H_2S is added by the bacterial decomposition of organic sulphur compounds, but this is a minor process and does not appreciably augment the small amount of iron sulphide formed by bacterial sulphate reduction.

These considerations help to explain why there is a poor correlation between reduced sulphur and organic carbon in freshwater sediments. Some examples are shown in figure 6. Regardless of how much organic matter is deposited, there simply is not enough sulphate available to form much pyrite. Consequently one observes low S values regardless of the level of organic carbon, and this result can be used to distinguish freshwater from marine environments. Above about 1 % C the ratio C:S for freshwater sediments is decidedly higher than that for normal marine (or euxinic) sediments (see figure 6).

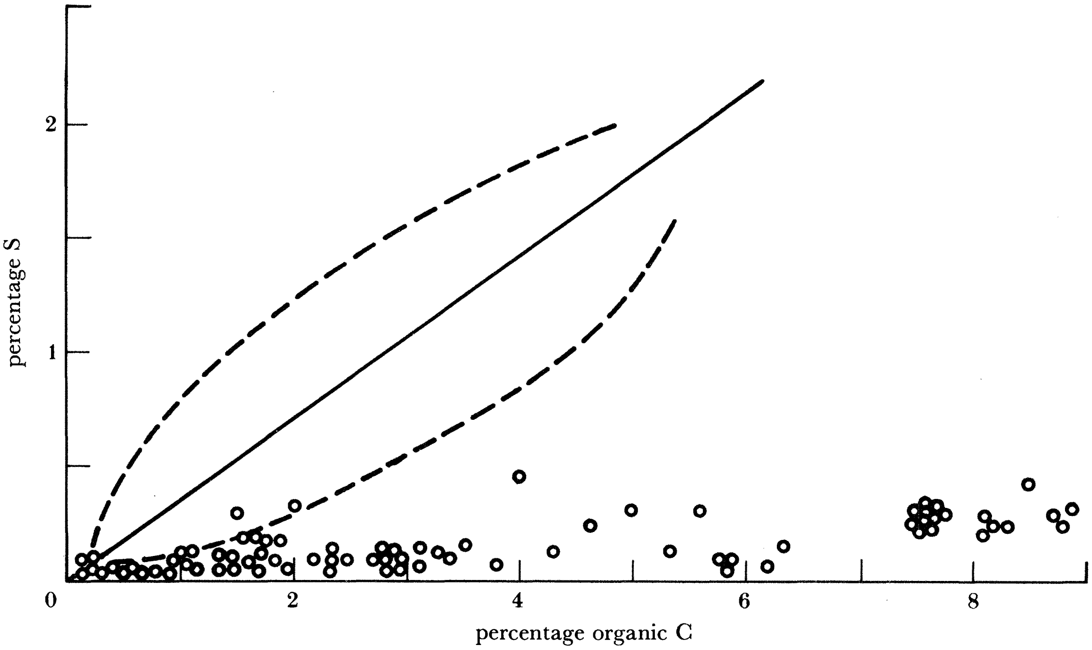

FIGURE 6. Plot of reduced sulphur (mainly pyrite) against organic carbon for freshwater lake sediments. Data for normal marine sediments from figure 4 are shown for comparison. After Berner & Raiswell (1983).

3. APPLICATION OF RESULTS TO ANCIENT ROCKS

(a) *Distinguishing palaeo-environments*

From earlier conclusions, it is obvious that C–S plots for rocks might be useful in helping to deduce whether organic matter was originally deposited under normal marine, euxinic, or non-marine freshwater conditions. Leventhal has recently found a method to distinguish euxinic from normal marine deposition by using C–S plots (Leventhal 1983*b*) and results agree well with independent criteria for euxinicity. Euxinic sediments can also be identified by a total lack of benthic fossils along with a lack of disturbance of fine sediment layers by bioturbation. This comes about because practically all benthic macro-organisms are killed by the H_2S present on euxinic bottoms. However, during the early Palaeozoic (and earlier periods) layer destruction by bioturbation was apparently rather limited even in normal marine environments (Larson & Rhoads 1983), so that at these times C–S plots should prove to be even more useful in helping to distinguish euxinic from normal marine environments.

The distinction of freshwater from normal marine (or euxinic) environments with the use of C–S plots is also possible. Berner & Raiswell (1984) show that organic-rich Carboniferous non-marine sediments, whose environment of deposition has been deduced independently on the basis of fossil and other evidence, can be distinguished from marine sediments on the basis of C:S ratios. Results are reproduced here as figure 7. In addition, use of measured C:S ratios by David Lawrence and Paul Olsen, both of Yale University, has proven useful in distinguishing Cretaceous marine from non-marine environments as well as for detecting saline phases of otherwise freshwater Triassic lakes (personal communication). From these results it is probable that C:S ratios should prove to be a helpful tool in deducing other ancient palaeo-environments.

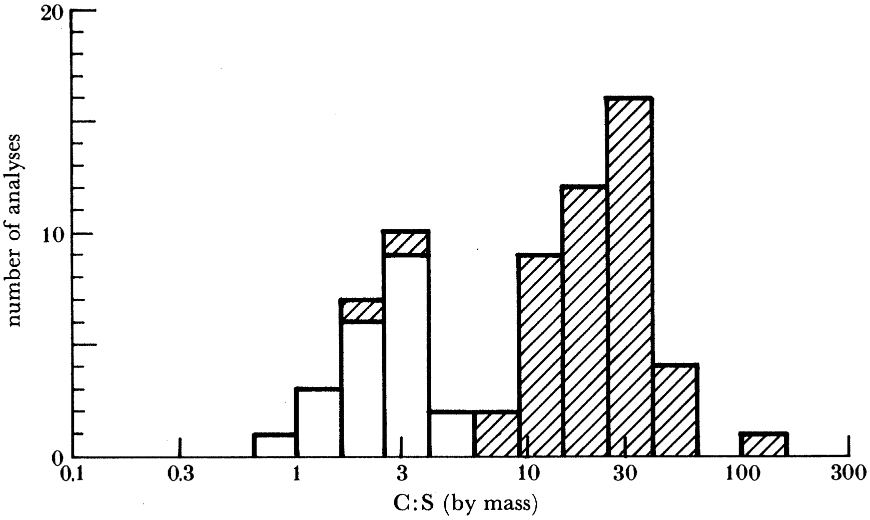

FIGURE 7. Histogram (on a logarithmic scale) of C:S ratios for marine (open) and non-marine (shaded) sediments from the same Carboniferous sections. After Berner & Raiswell (1984).

(*b*) *Change in environments over geologic time*

Even though most organic burial at present occurs under normal marine conditions, there is no reason to believe that burial on the continents in fresh water or in euxinic basins could not have been more important in the geologic past. That a shift in the relative importance of the three environments over Phanerozoic time actually took place can be shown through the use of data for the sulphur and carbon isotopic composition of palaeo-oceans as recorded by evaporites and limestones, respectively. Berner & Raiswell (1983), by using a modified version of the sulphur isotope mass-balance model of Garrels & Lerman (1981) (see also Garrels & Lerman 1984), have calculated that the worldwide average burial ratio of C:S for all sedimentary environments has changed over the past 600 Ma. Updated results, with the use of the ^{13}C and ^{34}S data reported by Lindh (1983) are shown in figure 8.

Berner & Raiswell (1983) interpret the large fluctuations over time in average C:S ratio in terms of different 'mixes' of euxinic (low C:S), freshwater (high C:S) and normal marine (intermediate C:S) organic matter burial. Low average C:S values during the early Palaeozoic can be explained by the much greater abundance of euxinic basins at that time, combined with very low burial of organic matter in fresh water caused by the lack of vascular land plants before the Silurian. The former is in keeping with the ubiquity of organic-rich, apparently euxinic shales (graptolite facies) deposited then (see, for example, Berry & Wilde 1978). Very high average C:S ratios during the Permo–Carboniferous, on the other hand, can be explained by

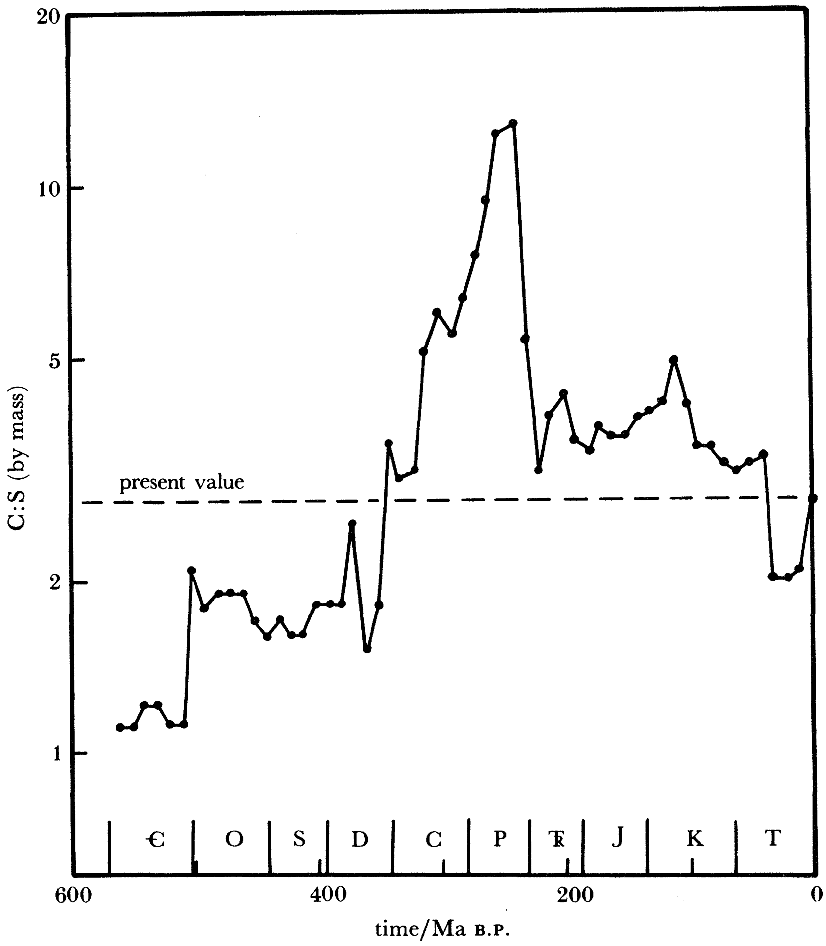

FIGURE 8. Plot of mean worldwide C:S ratio (on a logarithmic scale) for all sediments as a function of age. Results based on the theoretical model of Garrels & Lerman (1981, 1984) but by using independent calculations of organic carbon and pyrite sulphur burial. Data used in the calculations: present mass of pyrite sulphur = 255×10^{18} mol; present mass of $CaSO_4$ sulphur = 510×10^{18} mol; constant mass of oceanic sulphur = 38×10^{18} mol; $\delta^{34}S$ and $\delta^{13}C$ of ocean given in data compiled by Lindh (1983); present pyrite sulphur burial rate = 0.51×10^{18} mol Ma^{-1}; present $CaSO_4$ burial rate = 1.02×10^{18} mol Ma^{-1}; present organic carbon burial rate = 3.80×10^{18} mol Ma^{-1}. Method of successive steady states changing every million years.

much greater deposition of organic matter on land. This is in keeping, both qualitatively and quantitatively, with what is known about the worldwide abundance of organic matter in coal basins as a function of geologic age (Bestougeff 1980; Ronov 1976; for a summary and comparison of data see also Berner 1984). Enhanced deposition of organic matter in freshwater swamps and lakes should produce more coal and freshwater organics in general and involve the burial of less pyrite, thus leading to higher worldwide C:S ratios.

Further testing of these ideas is needed to see if the explanations offered for fluctuating C:S ratios are correct. An additional means of testing the ideas would be to ascertain whether burial of organic matter in normal marine environments was lower during the early Palaeozoic (because of greater worldwide euxinicity) and during Permo–Carboniferous time (because of greater burial on land) than it is today. This should be subject to testing. At any rate it shows that studies of modern sediments can be used to make major deductions about the environment of deposition of ancient rocks.

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Discussion

J. W. DE LEEUW (*Technical University, Delft, The Netherlands*). The organic component in sediments can react both with hydrogen sulphide and with other more reactive sulphur species such as polysulphides. Do these reactions compete with those involving iron, or are they only important in iron-free sediments?

R. A. BERNER. We have used a chromium reduction technique, which is specific to pyrite, to separate organic sulphur from that in pyrite and have found that more than 90 % of the sulphur in sediments from Long Island Sound and other near-shore environments is in the form of pyrite. Organic sulphur is present, but only in small quantities. Organic sulphur is likely to be much more important in freshwater sediments than it is in marine ones.

B. SPIRO (*Geochemistry Division, British Geological Survey, London*). In marine sediments that are rich in organic matter and poor in iron, such as limestones, reduced sulphur is likely to be incorporated in the organic matter. This process should lead to an enrichment of sulphur-containing compounds. There is some evidence that free sulphur is first formed by reduction, which then reacts with the organic matter. The behaviour of carbonate sediments is therefore rather different from those in which there is abundant iron.

R. A. BERNER I agree completely with these comments. The behaviour of sulphur is quite different in iron-poor rocks, where pyrite formation cannot remove the sulphur formed by sulphate reduction. In such rocks the organic sulphur may account for an appreciable proportion of the total sulphur content. In this respect biogenic sediments differ from terriginous sediments, in which there is abundant iron.

D. G. MURCHISON (*Organic Geochemistry Unit, University of Newcastle*). The times of occurrence of high C:S ratios correspond well with the major coal-forming periods during the Palaeozoic and Mesozoic. During the whole of the Tertiary, however, this ratio is lower than it is at the present time, yet the Tertiary was also a time of considerable coal formation. How does Dr Berner account for this observation?

R. A. BERNER. The proposed model depends on the carbon and sulphur isotopic composition of the oceans as recorded by marine limestones and evaporites respectively. Isotopic data for the Tertiary for sulphur are probably not as good as those for carbon and new data could change results. There is no doubt that during the early Tertiary carbon burial rates worldwide, as deduced from the carbon isotopic data, were higher than at present, which suggests greater burial on land, but further refinement of the sulphur isotopic record is needed before anything more can be said on this matter.

G. EGLINTON The variation of the C:S ratio with time implies that there are corresponding variations in the reservoirs of carbon and sulphur in the biosphere, hydrosphere and atmosphere. What can Dr Berner say about these variations?

R. A. Berner. In the model described here the sulphur and the carbon are coupled in such a way as to leave the atmospheric oxygen reservoir unaffected. There must be some such coupling, because otherwise the reduction of large amounts of sulphate to sulphide would lead to a large increase in atmospheric oxygen. Because high concentrations of oxygen are toxic to life, no such changes can have occurred during most of the Earth's history. Therefore sulphate reduction must in general be accompanied by carbon oxidation and this general correlation is clearly seen in the isotopic measurements. However, there are small detailed variations in carbon and sulphur isotopic ratios that are uncorrelated. Whether these variations are associated with variations in the amount of oxygen in the atmosphere or with variations in the ferrous:ferric ratio is not yet clear. Iron was not included in the model because the amount of oxygen required to change its oxidation state is only one eighth of that required to change sulphur from a sulphide to a sulphate. Though the abundances of iron and sulphur are similar, the importance of sulphur in the oxygen budget is, for this reason, much greater.