

STUDIES ON THE FORMATION OF  
PYRITE IN JURASSIC SHALES

A Thesis Submitted For The Degree Of Doctor Of  
Philosophy In The Faculty Of Science Of The  
University Of Leicester

By

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August 1983

## Chapters of Thesis Published as Papers

### Chapter 2

1986 Pyrite formation in bioturbated clays from the Jurassic of Britain.

Geochimica et Cosmochimica Acta Vol 50 pp517-523

### Chapter 6

1986 Pyrite replacement of mollusc shells from the Lower Oxford Clay (Jurassic) of England.

Sedimentology Vol 33 pp 575-585

### Chapter 5

with .I.D Hudson

1987 Pyrite formation in Jurassic shales of contrasting biofacies.

In *Marine Petroleum Source Rocks*. Ed Brooks, J & Fleet AJ

Geological Society Special Publication No26 pp69- 78

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STUDIES ON THE FORMATION OF PYRITE IN JURASSIC SHALES

Ian St John Fisher

Pyrite is a ubiquitous mineral in shales. It results from the bacterial reduction of seawater sulphate to sulphide and the reaction of that sulphide with iron to form iron sulphides and subsequently pyrite.

Five Jurassic shales were examined. 1 The Upper Oxford Clay (Oxfordian) Warboys Cambridgeshire. 2 The Dunans Clay (Callovian-Oxfordian) Isle of Skye. 3 The Lower Oxford Clay (Callovian) East Midlands. 4 The Posidonia Shales (Lias  $\epsilon$ ) Southern Germany. 5 The Dunans Shale (Callovian) Isle of Skye.

The five shale units are divisible into three major biofacies "Normal" (Units 1 & 2), "Restricted" (3) and "Bituminous" (4 & 5), which show varying pyrite contents and isotopic compositions, that reflect the changing influence of the three limiting factors of pyrite formation (sulphate, organic carbon, and iron).

Samples of shale were analysed for fine grained pyrite content and isotopic composition, organic and carbonate carbon, and hydrochloric acid soluble iron. The Normal shales showed low pyrite sulphur (<1.3%) and

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organic carbon (<2%), degree of pyritization (D.O.P.) (<0.5) and negative (<-28‰)  $\delta^{34}\text{S}$  values. These are consistent with the formation of pyrite near the sediment surface, limited by organic carbon. In the Restricted shales higher pyrite sulphur (av.1.4%) and organic carbon (av.5%), degree of pyritization (0.5 to 0.7) and less negative (>-28‰, <-9‰)  $\delta^{34}\text{S}$  values indicate the continuation of pyrite formation deeper into the sediment, where it is limited by sulphate diffusion. High D.O.Ps in the Posidonia Shales (>0.8) suggest that pyrite formation is limited by the availability of iron in Bituminous shales. Heavier  $\delta^{34}\text{S}$  values (>-28‰) in the Posidonia Shale suggest limitation of sulphate reduction by sulphate diffusion, and lighter values in the Dunans Shale (<-28‰) suggest limitation by organic matter.

Petrographic and isotopic studies of shell replacement and associated concretionary pyrite from the Lower Oxford Clay show types of replacement related to the differences between the porewaters within the shell and those of the shale, particularly as regards iron supply.



## Acknowledgements

My thanks go first and foremost to my joint supervisors, Drs J.D. Hudson and M.L. Coleman, who initiated this research project and who provided useful suggestions and encouragement throughout it. I would like to thank Prof. J. Tarney for the use of facilities at Leicester University and the Director of the Institute of Geological Sciences for the use of facilities at Grays Inn Road, London.

My thanks go to Keith Duff and Dave Martill who assisted me with sample collecting, to Wolfgang Küsspert, who provided me with samples and data for the Posidonia Shales.

I would like to thank the staff of the Stable Isotope Facility at Grays Inn Road for help and assistance with sulphur isotope determinations, particularly Marge Cox and John Rouse.

I am greatly indebted to George Saville who devised the experimental set up for Carbonate and Organic Carbon analysis.

I am grateful to London Brick Company P.L.C. for permission to collect from their pits, and to John Horrell their Chief Geologist.



## Acknowledgements

The technical assistance of several members of the Geology department Central photographic Unit, and Computer Laboratories is gratefully acknowledged, particularly Pat Gray and Murray O'Keefe for assistance in iron determinations, Rod Branson for help with photographic developing and printing, Sue Button for advice on and preparation of diagrams, George McTurk, who operated the the S.E.M., John Preston, Paul Ayto and Colin Cunningham, who made sections, and Dick Mobbs for assistance with the word processor.

For invaluable discussions , both geological and non geological, I would like to thank Richard Benmore, Chris Clayton, Costas Fotakis, Dave Martill, Cathy O'Brien, Mike Petterson and Richard Shaw, as well as several other fellow researchers in Leicester and London.

Finally, I wish to acknowledge the Financial assistance of a N.E.R.C. Case Studentship with the Institute of Geological Sciences, which enabled me to undertake this research.

## Introduction

### General Introduction.

Pyrite is a ubiquitous mineral in organic rich sediments and results from the anaerobic bacterial reduction of seawater sulphate, and the reaction of the sulphide produced with iron. The anaerobic reduction of sulphate is one of a series of diagenetic reactions which involves the combustion of organic matter by successively less efficient oxidizing agents (Curtis 1977).

In recent years many studies have been made of sulphate reduction in recent sediments and under laboratory conditions (See the work of Berner, Goldhaber, Kaplan, Sweeney, Chambers, Trudinger, and Others). These studies have revealed various of the factors which affect the formation of pyrite, chiefly organic carbon concentration, availability of iron and sulphate, rate of sedimentation, bottom water conditions and bioturbation. Many of the studies have concentrated on the variation of the stable isotopes of sulphur, as the bacterial reduction of sulphate is accompanied by a large but variable depletion in the  $^{34}\text{S}$  isotope. Because of the bacterial fractionation, enrichment of the  $^{34}\text{S}$  isotopes in pore water sulphate takes place, the continuing reduction of sulphate during burial in sediments can therefore be monitored. Goldhaber and Kaplan (1980), proposed a model for

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sulphur isotopic composition of fine grained pyrite in the sediments of the Gulf of California. This involved the division of sulphate reduction zone into two, an open system subzone and a partially closed system subzone. The model applies chiefly to sediments in which the reduction of sulphate is limited by the available sulphate. It has been found that the model is at least qualitatively applicable to ancient sediments.

Comparable studies of pyrite in ancient sediments are limited. Authors such as Maynard (1980) have attempted to apply some of the results from the work on recent sediments but with limited success. Other authors such as Coleman and Raiswell (1981), have dealt mainly with pyrite formation in concretions. Few concerted studies of the amounts and isotopic compositions of the general fine grained pyrite in ancient sediments have been undertaken.

Some work by Hudson (1982) on the pyrite in ammonite-bearing shales in England and Germany together with work on the isotopic compositions of the pyrite (Coleman and Hudson 1980) revealed a wide range of sulphur isotope compositions from fossils, concretions and the fine-grained pyrite. The work showed some associations between the types of pyrite, their isotopic composition and the environment of formation as revealed from palaeoecological studies. Their work formed the starting point for this study.

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For the purpose of this study five Jurassic shales were examined. These were:

1. The Upper Oxford Clay (Oxfordian), from Warboys brick pit, Cambridgeshire.
2. The Dunans Clay (Callovian-Oxfordian), from Staffin Bay on the Isle of Skye.
3. The Lower Oxford Clay (Callovian) from several brickpits in the East Midlands.
4. The Dunans Shale (Callovian), also from Staffin Bay.
5. The Posidonia Shale (Lias  $\epsilon$ , Toarcian) from southern Germany.

The five shale units are divisible into three main biofacies, based on the palaeoecological classification of Morris (1979, 1980). This classification is based on the types of bivalve molluscs present. These can be divided into groups on their mode of life (infaunal, epifaunal) and feeding (deposit, suspension). Morris showed that the classification corresponded with factors such as degree of preservation of lamination as compared with bioturbation. He also considered it to correlate with the presence of certain kinds of carbonate concretions.

Each shale unit was analysed for the fine-grained pyrite content and its isotopic composition, organic carbon and carbonate carbon, and HCl soluble iron. Samples of pyritized shells and concretions were collected from the

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Lower Oxford Clay and studied petrographically and analysed for their isotopic composition.

The thesis is set out in the following manner. Each chapter, except the final general conclusions, is written in the form of a paper. It may therefore be found that some repetition occurs in the introductory parts of various chapters.

Chapter 1 presents a review of experimental and recent sediment studies. It presents the factors and theories on which the interpretation on the data from the ancient sediments is based. The chapter commences with a section that places sulphate reduction within the general early diagenetic scheme. Then are considered some of the aspects of the microbiology of sulphate reducing bacteria and particularly their associated fractionation of the stable isotopes of sulphur. The next section investigates the pathway of pyrite formation as deduced from various inorganic chemical studies. The sources of iron are considered in this section. The next portion of the chapter considers aspects of the modelling of sulphate reduction in sediments. The separate problems of modelling sulphate reduction in the environments where bottom waters are oxic and the effects of bioturbating organisms must be taken into account, as compared to anoxic conditions where sulphate reduction



occurs in the water column are discussed. Resulting correlations between pyrite sulphur contents and organic carbon content, are considered. Finally the resultant sulphur isotopic effects occurring within the sediment and their relationship to the bacterial reduction and the diagenetic models of pyrite formation are described.

Chapter 2. deals with the formation of pyrite in the highly bioturbated "Normal" facies. The two units described are the Upper Oxford Clay and Dunans Clay. Details of the sections, the lithologies and the palaeoecology are given. The range and variations of the various measured quantities are given, and an assessment is made of the limiting factors of pyrite formation in the "Normal" facies. The Normal shales characteristically show low pyrite sulphur and organic sulphur contents, negative  $\delta^{34}\text{S}$  values and low and variable degrees of pyritization. These two shale units show the importance of bioturbation during the early diagenesis and its effect on the recycling of sulphide to sulphate in the surface sediment layers.

Chapter 3. deals with the formation of pyrite in the Lower Oxford Clay, which belongs to the "Restricted" facies of Morris. Use is made of the more detailed palaeoecological classification of Duff(1975). The variations of pyrite sulphur content, carbonate and

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organic carbon and  $\delta^{34}\text{S}$  are recorded for various of Duff's biofacies. The first three components are found to vary in association with the biofacies. Steady state models, discussed in Chapter 1, and the predicted sulphur isotopic compositions are used to demonstrate a limitation of pyrite formation by sulphate and to explain the isotopic values of the fine-grained pyrite. Consideration is given to the sulphur isotopic composition of shell replacement and concretionary pyrites which show distinctly heavier  $\delta^{34}\text{S}$  values compared to the fine grained pyrite. This appears to relate to the distinct microenvironment presented by shells and to the times and phases of replacement as revealed in the petrographic study described in chapter 6.

Chapter 4 considers the Posidonia and Dunans Shales. Both of these are thought to have been deposited in anoxic bottom waters, and correspond to the "Bituminous" facies of Morris. Aspects of the supposed environments of deposition which would be thought to affect the formation of pyrite are examined. The two shales although belonging to the same broad biofacies are found to have distinctly different  $\delta^{34}\text{S}$  pyrite compositions and organic carbon to pyrite sulphur ratios. The results of the HCl soluble iron suggest that one of the main limitations of pyrite

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formation in the "Bituminous" shale facies is the availability of iron. The results seem to indicate that sulphate reduction (as opposed to pyrite formation) is limited in the Posidonia Shales by sulphate and in the Dunans Shales by organic carbon. It is this distinction which leads to the different  $\delta^{34}\text{S}$  values, the more positive in the Posidonia Shale and the more negative in the Dunans Shales. The results from the Posidonia Shale suggest a compromise for the more extreme interpretations of its environment of deposition particularly those suggesting large degrees of stagnation of the water column.

Chapter 5 This chapter has been co-written with Dr J.D. Hudson and submitted to the Geological society of London Special Publication on Marine Petroleum Source Rocks. The results and their interpretation are Fisher's; Dr Hudson assisted with the general set out of the paper, the introduction and the general conclusions. It constitutes a compilation of the data from Chapters 2,3 and 4 and points out the differences in the data between the facies. It indicates how the factors which affect the formation of fine grained pyrite vary between the facies and how a combination of the pyrite sulphur content and the  $\delta^{34}\text{S}$  can be used to distinguish the facies. The chapter concludes on the use of the  $\delta^{34}\text{S}$  values and the pyrite content to assess the



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favourability of organic matter burial and preservation in the three biofacies, from the point of view of petroleum source rock studies.

Chapter 6 is slightly separate from the other chapters as it is a petrographic study of the pyritic replacement of mollusc shells in the the Lower Oxford Clay. The chapter describes the material and the types of preservation found in both shell beds and large pyrite concretions around macro-conch ammonites. Assessment of the phases and times of replacement is made. The role of the chemistry of the replacement on the structures and textures is considered. Some reference is made to the isotopic data of Chapter 3.

Chapter 7. This chapter summarizes the major conclusions of the thesis.

Appendix. A detailed description of the method of Carbon and Carbonate analyses, which is a modification of that of Bush (1970) by G.W.Saville, the former Geochemistry Technician at Leicester.

## Chapter 1

### A Review of Bacterial Sulphate Reduction and the Formation of Pyrite.

#### 1. Introduction.

The formation of pyrite in shales is one consequence of the bacterial reduction of seawater. Experimental data on the functioning of sulphate reducing bacteria have enabled some of the controls and consequences of sulphate reduction to be better explained and in some cases quantified. In ancient sediments it is not possible to track the the pathway of sulphate reduction and pyrite formation as in recent sediments. It is therefore only by analogy with recent sediments that the early diagenetic history of ancient sediments can be fully unravelled. This introduction is a review of the processes of bacterial sulphate reduction. Particular emphasis is put on the relationship between the total amount and isotopic composition of pyrite formed to the organic carbon input, the available iron and the role of organisms in the sediment.

#### 2. Diagenetic Zonation

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Sulphate reduction belongs to a series of diagenetic transformations that occur in sediments. On deposition unstable components of the sediment react (often due to the intervention of micro-organisms) and parameters such as Eh and pH reflect something approaching steady state activity in a dynamically reacting system. The most important diagenetic reactions involve the oxidation of organic matter. Consequences may include the formation of pyrite, phosphate, carbonate, and chert. Curtis (1977) proposed that in marine sediments there are several diagenetic zones, at successive depths in the sediment, which represent differing styles of microbial organic metabolism. These zones are summarized in Table (1). To the standard Curtis zone is added a further zone the post oxic zone (Berner 1981) which lies between the aerobic and sulphate reducing zone, and although in organic rich sediments is generally very thin it represents an important boundary between the two major zones. The succession of zones represents the use of less efficient oxidizing agents, when the previous more efficient oxidizing agents have been consumed. The quoted values of  $\Delta G_o$  (the Standard free energy change for the reaction) (Berner 1980) show the relative efficiency of the various reactions,  $\Delta G_o$  decreasing at each successive stage. The reduction of iron and manganese is shown in brackets because, although thermodynamically the

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reduction occurs in the Post oxic zone, iron and to a lesser extent manganese may persist metastably to be reduced in succeeding zones. Following each stage the remaining organic matter becomes more refractory.

The quantity and quality of organic matter surviving each zone, and ultimately passing into the hydrocarbon window, is dependent on the extent of diagenetic alteration occurring in each zone. Curtis (1977) and Coleman et al (1979) considered that the extent of degradation was dependent on the time spent in each zone, and hence that rate of burial was an important control. Coleman et al (1979) diagrammatically summarized (Fig 1) the effect of sedimentation rate on the diagenetic degradation of organic matter and the resulting prospect for oil generation.

The distribution of zones in natural environments is not always that of discrete successive layers in the sediment. Bioturbation (which will be discussed later) serves to mix the oxic, post oxic, and sulphate reducing zones. The transition from oxic to post oxic to sulphate reducing may occur not in the sediment, but in the overlying water column.

### 3. Bacterial Sulphate Reduction

The chief source of reduced sulphide in sediments is the bacterial reduction of seawater sulphate. Organic bound sulphur does not contribute significantly and

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generally makes up less than 10% of the total reduced sulphur in the sediment (Kaplan et al 1963, Hartman & Nielsen 1969). Sulphate-reducing bacteria therefore play an important part in the trapping of sulphur in sediments. Postgate (1979) in his book gives a good review of the microbiology of sulphate-reducing bacteria.

### 3.1 Sulphate-Reducing Bacteria.

The term Sulphate-reducing bacteria applies to a class of microbes which conduct dissimilatory sulphate reduction, that is they use sulphate as an oxidizing agent during respiration. They are strict anaerobes and become dormant in the presence of oxygen. There are two well established genera Desulfovibro and Desulfotomaculum. These bacteria have a wide tolerance of environmental conditions.

Sulphate-reducing bacteria have been found at a wide range of temperatures, in highly saline Antarctic lakes at  $-40^{\circ}\text{C}$  and under pressure at  $104^{\circ}\text{C}$ . Two forms of the bacteria exist, the normal mesophilic Desulfovibro and the thermophilic Desulfotomaculum. The mesophilic strains have an upper temperature limit of  $45-48^{\circ}\text{C}$ , but can, under laboratory conditions, be trained to tolerate  $50^{\circ}\text{C}$ . The thermophilic strains have an optimum at about  $60^{\circ}\text{C}$  and a lower temperature limit of about  $35^{\circ}\text{C}$ . Both barotolerant and barophilic strains of Desulphovibro



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are found. The later are found in deep ocean trenches. The bacteria have a wide tolerance of salt and are found in environments ranging from salt lake to fresh water, though the same strains are not found in both. In nature above about 2% NaCl the population consists almost entirely of Desulfovibro; Desulfotomaculum, except for one known occurrence, is not present in marine or other saline environments.

Although tolerant of a wide range of environments it appears that sulphate-reducing bacteria use a very narrow range of substrates for growth. A few C3 and C4 substituted fatty acids, such as lactate, pyrvate, fumerate and malate are used. Some strains can apparently use carbohydrates such as glucose and sucrose. The use of acetate and butyrate is limited to one strain, Desulfomaculum acetoxidans. The utilization of hydrocarbons by sulphate reducing bacteria is much debated. They may serve as energy sources, but not growth substrates. The presence of other assimilatable organic compounds is necessary for the bacteria to grow. Devol and Ahmed (1981) suggested that high rates of sulphate reduction in the Saanich Inlet resulted from the use of methane by the bacteria. They were unsure , though whether they employed it directly or indirectly via reactions coupled with other substances.

### 3.2 Rates Of Bacterial Sulphate Reduction.

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From experimental studies various factors have been identified as affecting the rate of bacterial sulphate reduction.

### 1. Sulphate Concentration.

Postgate (1951), Harrison and Thode (1958) and Kaplan (1962) found that above 10mmolar the rate of sulphate reduction was independent of sulphate concentration. From marine muds Benninger and Berner (reported in Goldhaber and Kaplan 1974) have shown sulphate independent rates of reduction down to 2mmolar. Nakai and Jensen (1964) carried out a prolonged experiment over 65 days and suggested that the results indicated first order kinetics with respect to sulphate. Sakai (reported in Goldhaber and Kaplan, 1974) indicated that the data could be reinterpreted in terms of zero order kinetics but with  $K$  (rate constant for sulphate reduction) becoming non linear at low concentrations. Rees (1973) suggested that the uptake of sulphate occurred via an organic complexing of the sulphate and not by simple diffusion, therefore when sulphate is present at sufficient concentrations to saturate the activation sites the rate of uptake is independent of sulphate concentration and zero order kinetics apply. At the concentration of sulphate in seawater (28mmolar) the sulphate uptake should proceed via zero order kinetics.

### 2. Organic Substrate.

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In experiments various hydrogen sources have been used for bacterial sulphate reduction, these include organic compounds and hydrogen. For the purposes of this study only those experiments involving organic donors are relevant.

Both the concentration and the type of organic matter have an effect on the specific rate of reduction (moles/ time /unit cell). Harrison and Thode (1958) demonstrated, with lactate as the substrate, that an increase in concentration resulted in an increased rate of reduction. Kaplan and Rittenberg (1964) found a variation of some 50x in the rate of reduction by varying the organic electron donor. Postgate (1979) (see above) indicates that the range of organic molecules utilized during growth is limited, therefore the use of less metabolisable organic compounds, such as alcohol in the Kaplan and Rittenberg experiments, leads to much slower rate of reduction.

### 3. Cell Growth.

Harrison and Thode (1958) showed that actively growing cells carried out sulphate reduction at a faster specific rate than resting cells.

### 4. Temperature and Pressure.

As stated above sulphate-reducing bacteria can withstand a wide range of temperatures and pressures. The effects of temperature and pressure on rate of reduction depend greatly on the strain of bacteria and the temperatures



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and pressures to which they are acclimatized. Harrison and Thode (1958) found that bacteria acclimatized to a given temperature showed much the same rate of reduction as bacteria acclimatized at another temperature. If bacteria acclimatized at a higher temperature are subjected to a lower temperature, Harrison and Thode found that a drop of  $10^{\circ}\text{C}$  resulted in a factor of 5 decrease in the rate of reduction. Data on the effects of pressure are scarce. Jannasch et al (1971) suggested that rate of reduction decreased with increasing pressure. The effect of pressure will, as with temperature, depend on the strains involved. As in nature the bacteria should be acclimatized to the pressure and temperature of the environments in which they live, the variation in temperature and pressure between environments should not have a great effect on the observed specific rates of reduction. Within any particular environment seasonal variations in temperature may have marked effects on the rate of reduction. For example the the sediments of Long Island Sound show a seasonal variation in temperature between  $2^{\circ}\text{C}$  and  $22^{\circ}\text{C}$  and a corresponding variation in rates of reduction of some 6 to 8x (Aller, 1977).

Many of the experiments dealing with rates of sulphate reduction have dealt also with the link between it and the fractionation of stable isotopes of sulphur between sulphate and sulphide.

### 3.3 The Kinetic Isotope Effect During Bacterial Sulphate Reduction

It has long been established that sulphate-reducing bacteria are capable of selectively metabolising the stable isotopes of sulphur. Sulphur has four stable isotopes with the following approximate abundances,

$^{32}\text{S}$	95%
$^{33}\text{S}$	0.77%
$^{34}\text{S}$	4.2%
$^{36}\text{S}$	0.017%

The ratio  $R$  of the two most abundant isotopes  $^{34}\text{S}/^{32}\text{S}$  is normally measured and expressed in the  $\delta$  notation.

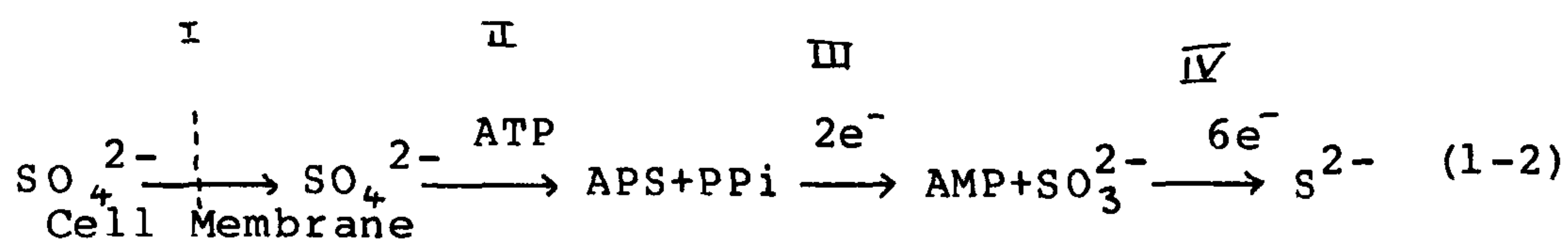
$$\delta^{34}\text{S} (\text{‰}) = \frac{(R_{\text{sample}} - R_{\text{standard}}) \times 1000}{R_{\text{standard}}} \quad (1-1)$$

The standard is the troilite sulphur from the Canon Diablo meteorite which has an isotopic ratio  $^{34}\text{S}/^{32}\text{S} = 0.450045$  ( $^{32}\text{S}/^{34}\text{S} = 22.220$ ) (Ault & Jensen 1962). The range of fractionations found during the production of sulphide by dissimilatory sulphate-reducing bacteria in laboratory experiments is +3 to -46‰, relative to the initial coexisting sulphate. Fig (2) shows a plot of fractionation vs specific rate of reduction. It can be seen that the largest fractionations are associated with the lowest specific rates of reduction. The bacterial

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reduction of sulphate can be viewed as a multi-stage metabolic pathway (Rees 1973), each stage involving an isotopic fractionation which may contribute to the overall fractionation. The overall fractionation depends on relative importance of each step and therefore on the functioning conditions of the bacteria.

Below is shown an idealized version of the metabolic pathway of sulphate reduction (Eq 1-2).



ATP = Adenosin 5-Triphosphate

AMP = Adenosin 5-Phosphate

APS = Adenylsulphate

PPi = Pyrophosphate

Steps I & II represent the uptake of sulphur by the cell and its activation. As seen above about 2mmolar sulphate does not affect the rate of reduction. Below this concentration all the sulphate entering the cell is subsequently reduced and the uptake of sulphur will control the overall fractionation. Harrison and Thode (1958) demonstrated that the minimum fractionation +3‰ resulted at low concentrations of external sulphate. The uptake of sulphate by E. coli and Saccharomyces cerevisiae leads to a minimum fractionation of -2.8‰ Kaplan and Rittenberg (1964). When sulphate is limited

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but other nutrients are still abundant, the uptake of sulphate is rate limiting and leads to an overall fractionation of  $\pm 3\%$ .

Step III Reduction of activated sulphate to sulphite.

Inorganic reduction of sulphate to sulphite leads to a fractionation of  $-22\%$  (Harrison and Thode 1957). In their experiments, Harrison and Thode (1958) found that under various conditions (changing temperature, nutrient concentrations, growth) the maximum fractionation was  $-25\%$  at the slowest rates of reduction. This compared favourably with the value of  $-22\%$  and they therefore concluded that under normal conditions the rate determining step was the reduction of sulphate to sulphite, followed by a rapid reduction of sulphite to sulphide. Chambers and Trudinger (1979) suggest that fractionations of between  $-22$  to  $-25\%$  at this stage may be an overestimate. The highly acid conditions of inorganic reduction are distinct from those of bacterial systems and APS is the substrate for biological reduction and not sulphate. With organic electron donors a minimum fractionation of  $-9$  to  $-10\%$  results (fig 3). Kemp and Thode (1968) found a fractionation of  $-9$  to  $-15\%$  between sulphate and sulphite using cell free extracts. Chambers et al (1976) using six different species of bacteria, both Desulfovibro and Desulfotomaculum growing in batch cultures under optimum

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conditions found the fractionation factor was  $-14.6 \pm 4\%$  and that this was independent of temperature, electron donor, or extent of sulphate reduction. These results suggested that the fractionation was associated with step *III* and was a function of the S-O bond in APS or of the enzymic mechanism of APS reduction. Chambers and Trudinger conclude from these data that the bacterial reduction of sulphate to sulphite has an isotopic effect of  $-10$  to  $-15\%$ .

### Step *IV* Reduction of sulphite to sulphide.

Rees (1973) suggested, by analogy with the chemical S-O bond breaking, that the reduction of sulphite to sulphide occurred with a fractionation of  $-25\%$ . Kemp and Thode (1968) reported a constant fractionation of  $-19.4\%$  during sulphite reduction by cell free extracts at pH 6. A single determination at pH 8 yielded a value of  $14\%$ , suggesting that the fractionation is pH linked. Chambers and Trudinger (1979) therefore suggest that a suitable value for the bacterial reduction of sulphite to sulphide lies between  $-14$  and  $-19\%$ .

The overall fractionation factor for bacterial reduction of sulphate to sulphide is dependent on the fractionation factors and the relative rates of forward and backward reactions at each stage. Rees (1973) demonstrated that the overall fractionation factor " $\alpha$ "



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(= {32S/34S sulphide}/{32S/34S sulphate}) is given by the expression

$$\alpha = \alpha_1 + (\alpha_2 - \alpha_1)X_1 + (\alpha_3 - \alpha_2)X_1X_2 + (\alpha_4 - \alpha_3)X_1X_2X_3$$

$\alpha_1$  and  $\alpha_{-1}$  etc. are the fractionations for the forward<sup>(1-3)</sup> backward reactions and  $X_1$  etc are the ratios of

of backward to forward reactions at steps I to IV. Rees (1973) assumed that on the forward steps I, III, and IV involved fractionations. This simplifies the equation to

$$\alpha = \alpha_1 + \alpha_3X_1X_2 + \alpha_4X_1X_2X_3 \quad (1-4)$$

If the fractionations adopted by Rees (1973)  $\alpha_1 = 0.997$ ,  $\alpha_3 = 1.025$ ,  $\alpha_4 = 1.025$  are assumed, then under condition where sulphate uptake is limiting steps II, III and IV occur very rapidly and the resulting fractionation is +3‰. Under normal experimental conditions when sulphate is not limiting the rate limiting step is the reduction of APS to sulphite and the reduction of sulphite to sulphide occurs rapidly so that sulphite does not build up and  $X_3 = 0$ . These conditions yield a fractionation between 0 and -25‰. At slow rate of reaction the reaction of sulphite to sulphide is sufficiently slow to allow the build up of sulphite and  $X_3 > 0$  allowing a further fractionation of -25‰. Rees nicely explains the range of fractionations seen in the laboratory, but, as seen above, Chambers and Trudinger cast doubt on the fractionations chosen at each step. The maximum

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fractionation allowed by their preferred values is -34‰, well short of the -46‰ reported from experiment. The maximum fractionation of -46‰ still stands even if it can not, as yet, be satisfactorily explained. One suggested explanation is that isotope exchange occurs between sulphate and sulphide. At equilibrium the fractionation between sulphate and hydrogen sulphide at 25 °C is -74‰ (Tudge and Thode 1950). Trudinger and Chambers (1973) suggested that the reaction pathway in Desulphovibrio is reversible. Chambers (1975) suggested that a fractionation of -19‰ in the absence of net sulphate reduction in a sealed culture of D. desulfuricans might have been due to isotopic exchange. Further work by Chambers et al (1976) did not support these results. Therefore theoretically such exchange reactions are possible and might at extremely slow rates of reduction lead to fractionations of -70‰ but are not experimentally substantiated.

### 4.1 Chemical and Textural Indications of the Pathway of Pyrite Formation.

In marine sediments one result of sulphate reduction is the formation of pyrite. Pyrite is a stable mineral in the absence of air and the presence of

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dissolved sulphide. Fig (4) shows the stability field of various iron minerals on a Eh pS diagram.

Laboratory experiments and studies on recent sediments have shown that pyrite is not normally the first formed iron sulphide. Goldhaber and Kaplan (1974) give a good review of the experiments and the resulting products. Fig (5) shows the supposed pathway of pyrite formation from Goldhaber and Kaplan (1974). The initial iron sulphide formed is normally mackinawite (tetragonal FeS soluble in HCl). This is often poorly crystalline and occurs as a black amorphous precipitate (Sweeney and Kaplan 1973). The iron monosulphide is converted to the bisulphide (pyrite) by the addition of elemental sulphide ( $S^0$ ) either directly or via other iron sulphides such as greigite ( $Fe_3S_4$ ). Table 2. shows the condition and products of various experiments on iron sulphide formation. Different pathways of pyrite formation can result in distinct morphologies, particularly the framboidal texture.

Sweeney (1972) and Sweeney and Kaplan (1973) demonstrated that the framboidal texture resulted from the conversion of monosulphide to greigite, when the spherical texture results and the transformation of greigite to pyrite in which the spherical texture is retained or changed due to the internal nucleation of pyrite to form framboids. The experiments were undertaken in both hydrous and anhydrous condition



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indicating that the spherical form was a property of the solid greigite and not a gel like structure as had been suggested by Schouten (1946). Fig (6) indicates the pathway of framboidal pyrite formation. If the conversion of monosulphide to pyrite proceeds without the intervention of greigite then monocrystalline pyrite should result.

In certain circumstances pyrite may precipitate directly from solution without any intermediary iron sulphide. From the experiments of Berner (1964), Rickard (1969) and Roberts et al (1969) where goethite was reacted with  $H_2S$  at  $pH < 6.5$  . pyrite was invariably present as a product, and acid volatile iron monosulphide was only a minor constituent or absent. This is thought to be due to the effects of pH on the solubility products of pyrite and mackinawite. Above pH 6.5 both are supersaturated but mackinawite precipitates more rapidly than pyrite. Below pH 6.5 mackinawite becomes undersaturated and pyrite can precipitate without competition. From studies of the Jet Rock concretions, Raiswell (1982) considered that the euhedral pyrite formed after an initial framboidal phase, and resulted from a limitation of iron. This caused mackinawite to become under saturated and allowed pyrite to precipitate directly in a euhedral form.

The transformation of Mackinawite  $\longrightarrow$  Greigite  $\longrightarrow$  Pyrite require successive addition of elemental

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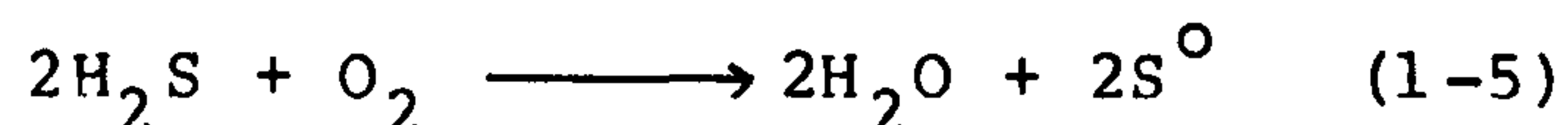
sulphur. Berner (1970) demonstrated that the reaction proceeded by the addition of sulphur and not the removal of iron. The elemental sulphur is produced by the reoxidation of sulphide. This may result in three ways:

1. by the action of aerobic sulphur oxidizing bacteria at the oxic/anoxic boundary,

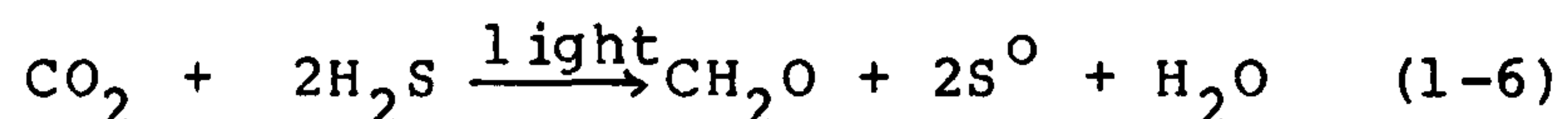
2. by the action of anaerobic photosynthetic sulphur-oxidizing bacteria utilizing  $\text{CO}_2$ ,

3. by the reaction of sulphide with ferric iron.

Sulphide oxidizing bacteria are either aerobic or anaerobic and photosynthetic. In the former case the reaction occurs as follows,



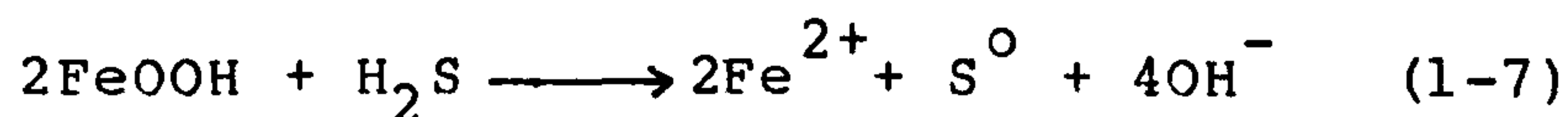
in the latter case,



In deep anoxic conditions neither of these kinds of bacteria can function in the sediment, either due to lack of oxygen or lack of light. Any bacterial sulphide reoxidation that does occur must take place at the redox boundary in the water column. The sulphur formed may be distributed by currents and settle to the bottom (Ostroumov et al 1961). When the sediment surface is aerobic the bacteria may function without difficulty and elemental sulphur is formed within the sediment.

Elemental sulphur may also be formed by the reaction of  $\text{H}_2\text{S}$  with goethite or some other ferric iron

compound, e.g.



### 4.2. Sources of Iron.

Sulphate reduction is dependent primarily on the availability of sulphate and organic carbon, but for the sulphide that is produced to be represented in the sediment it must be trapped as some metallic sulphide, the most common in ancient sediments being pyrite. The presence of iron is a necessary prerequisite for the formation of pyrite. Iron is commonly incorporated in the sediment as detrital phases such as augite, magnetite, hornblende, goethite, and hematite. A large quantity of iron is associated with the clay fraction (Carroll, 1958).

1. As an essential constituent of the clay lattice in nontronite, chlorite, vermiculite, chamosite and glauconite.
2. As minor isomorphous substitutions in the lattice.
3. As oxide coatings on the grains .

Resistance of the various minerals to reaction with hydrogen sulphide is variable. Berner (1970) found that hydrogen sulphide is more reactive to fine grained hematite, goethite and chlorite and less reactive to sand and silt sized magnetite, hornblende , goethite, biotite, augite, and epidote. The most easily utilized source of iron in sediments is the oxide coating on

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grains.

The oxide coating on the mineral grains contain iron in the ferric form which must be reduced prior to incorporation in pyrite. This may occur with hydrogen sulphide as the reducing agent, in which case the ferric iron is reduced and simultaneously iron sulphide is precipitated. Iron may also be reduced by the reaction with various organic compounds.

The role of iron as a limiting factor in pyrite formation was discussed by Berner (1970), who defined a function Degree of Pyritization (D.O.P.).

$$D.O.P. = \frac{\%Fe \text{ as Pyrite}}{\%Fe \text{ as Pyrite} + \%Fe \text{ soluble in HCl}} \quad (1-8)$$

The %Fe soluble HCl is determined by boiling the sediment for 1 min in 12N HCl. The iron liberated is a measure of the iron still present that could react with hydrogen sulphide. Berner found the solubilities of iron minerals in HCl to be similar to their reactivity with hydrogen sulphide. The high concentration of HCl used may lead to the solubilization of greater quantities of iron than would react with the normally low concentration of hydrogen sulphide present in sediments.

Hence the HCl soluble iron is only a guide to the available iron, giving a maximum value for %Fe HCl, and a minimum value for D.O.P. The value for D.O.P. theoretically lies between 0 and 1 although for the

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reasons given above the value of D.O.P. is unlikely to actually reach 1. For coastal sediment from Connecticut Berner found D.O.P. did not exceed 0.4 and concluded that iron was not, in that case, limiting pyrite formation. Berner suggested though that in conditions where high concentrations of hydrogen sulphide occur, iron may become limiting in sulphate reduction and high D.O.P.s result.

### 5. Models of Sulphate Reduction In Sediments

Studies on recent sediments have led authors to formulate models for the reduction of sulphate in sediments. These describe the porewater sulphate profile and the build up of iron sulphide in the sediment. For the purposes of describing models of sulphate reduction it is worth separately considering environments in which the benthic waters are anoxic and those in which they and the surface layers of the sediment are oxic. This is mainly because of the strong influence that benthic organisms have on the physical and chemical properties of the surface sediment layers in which they live.

#### 5.1 Sulphate Reduction in sediments from oxic environments



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The zone of sulphate reduction in sediments with oxic surface layers may be divided into two parts;

- a. An upper bioturbated zone
- b. A lower zone in which solute movement occurs by diffusion.

Henceforth the former will be termed the "zone of Bioturbation" and the latter the "Zone of Diffusion".

### 5.1a Diagenesis in the Zone of Bioturbation.

In conditions where the benthic waters are oxic the surface layers of the sediment (upto 1m or so )are subjected to the action of benthic organisms. The bioturbation produced from the action of these organisms alters the chemical and physical properties of the sediment. Some aspects of this have been studied in detail by Aller(1977) and the effects of bioturbation in the recent sediments of Long Island Sound (U.S.A.) are considered by Goldhaber et al (1977).

The influence of various organisms on the sediment is related to their mode of life and method of feeding. Sedentary tube dwelling organisms can move large quantities of oxygenated seawater through their burrows and in so doing alter the pattern of diffusion in the sediment, essentially placing deeper parts of the sediment in contact with the overlying seawater. The burrow structures effect the distribution of organic matter in the sediment, the mucus rich wall acting as an



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organic rich site for microbial action, particularly sulphate reduction (Aller 1977). Mobile infaunal deposit feeding organisms, such as protobranchs, move rapidly through the sediment and homogeneously rework it. The result of this is to enhance the migration of ions over that for normal diffusion.

Within the bioturbated layer oxic and anoxic environments may exist side by side. Burrowing organisms can maintain oxic conditions in their burrows in essentially anoxic sediments by pumping large quantities of seawater through them. In generally oxidising surface layers sulphate reduction may occur in micro-reducing environments, such as faecal pellets, burrow walls, or enclosed voids such as foram tests (Kaplan et al 1963, Goldhaber et al 1977).

In the surface layers the combination of oxic and anoxic environments, and the constant reworking of the sediment produces conditions in which sulphate reduction occurs and its products,  $H_2S$ ,  $FeS$  and  $FeS_2$  can be reoxidised. Aller (1977) indicates that upto 60% of the total sulphate reduced may be lost due to reoxidation. Such reoxidation is indicated in Aller's study by the sharp  $Fe^{2+}$  spikes in the concentration profile, due to the net reoxidation of iron sulphide at that level.

The irrigation and reworking of the sediment although reducing concentration gradients does not always dominate them; if such was the case then solute

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concentrations in the zone of bioturbation would be constant at their seawater values. Deviations from constant depth/concentration profiles, such as the  $\text{Fe}^{2+}$  spikes are often seen (Aller 1977, Goldhaber et al 1977).

The total amount of iron sulphide formed in the zone of bioturbation will equal the total amount of sulphate reduced less that reoxidized, assuming that sufficient iron is present to trap the sulphide formed.

The total amount of sulphate reduced will depend on

1. The input of metabolisable organic matter to the sediment.
2. The relative rates of aerobic and anaerobic metabolism.
3. The residence time of the sediment in the zone of bioturbation.

The input of organic matter is important as it controls the rate and amount of sulphate reduction occurring. The relative rates of aerobic and anaerobic metabolism affect the proportion of the initial organic supply which is metabolised by sulphate reducing bacteria. This is due to the mixed oxic/anoxic nature of the sediment in which there will be competition for the organic matter between the two types of bacteria. This component will depend on the distribution of oxic and anoxic microenvironments and, hence, the extent and style of bioturbation. The amount of sulphate reduced is directly dependent on the residence time of the sediment in the

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zone of bioturbation as would be expected. The residence time itself will depend on a) the rate of sedimentation and b) the thickness of the zone. The faster the rate of sedimentation and the thinner the zone the less time the sediment spends in it.

The extent of reoxidation will depend on two factors.

1. The nature and mobility of the bioturbating organisms.

2. The time spent in the zone.

Both of these factors affect the extent of exposure of the iron sulphide products to oxidizing conditions, the former by influencing the proportion of oxic micro-environments and the reworking of sulphide into them. The time spent in the zone is, as in the case of reduction, dependent on sedimentation rate and thickness of the zone, such that faster sedimentation rate and thinner bioturbation zone leads to less sulphide reoxidation. This works in the opposite sense to sulphide reduction, as although longer residence times lead to more sulphate reduction, it also leads to more reoxidation. Thus in considering the total amounts of iron sulphide formed, slow sedimentation rates and thicker bioturbation zones are partly offset by greater amounts of reoxidation.

The proportion of the initial organic input surviving the zone of bioturbation is dependant on the

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residence time of the sediment in the zone. The longer the time spent in the zone the more opportunity there is for the oxidation of the organic matter by the aerobic and anaerobic bacteria. As the bacteria preferentially consume the more metabolisable organic fractions, the surviving organic matter is more refractory.

A relationship exists between the extent of degradation in the zone of bioturbation and the metabolisability of the surviving organic matter. Toth and Lerman (1977) found a relationship between the first order rate constant for sulphate reduction ( $K$ ), at the base of the zone of bioturbation, and the rate of sedimentation ( $W$ ).

$$K = AW^2 \quad (1-9)$$

$A$  is an empirical constant  $= 0.04 \text{ yr/cm}^2$  derived from fig (7).

As the rate constant  $K$  is essentially a measure of the metabolisability of the organic matter and the residence time in the zone of bioturbation is inversely proportional to the rate of sedimentation, the Toth and Lerman formula represents a relationship between extent of oxidation and time spent in the zone of bioturbation. When the degradation of organic matter in the zone of bioturbation is large then the surviving organic matter

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may be totally unmetabolisable and sulphate reduction will not continue any deeper in the sediment. Any surviving metabolisable organic matter is available for the reduction of sulphate diffusing into deeper parts of the sediment.

### 5.1b Sulphate Reduction in the Zone of Diffusion

Below the zone of active mixing sulphate is supplied to the sediment by diffusion. The reduction of the sulphate has been modelled by Berner (1964,1971, 1974,1980) using steady state principles. The model is based on the following assumptions:

1. Organic matter decomposition follows first order reaction kinetics.
2. The only chemical reaction affecting sulphate in pore water is bacterial reduction.
3. Adsorption of sulphate is negligible.
4. Compaction, water flow, porosity gradients etc can be ignored.
5. Diffusion occurs by molecular processes only.
6. Steady state diagenesis occurs.

The resulting diagenetic equations are:

$$\begin{array}{l} \text{(For Sulphate)} \end{array} \quad D_s \frac{\partial C}{\partial x^2} - W \frac{\partial C}{\partial x} - LFKG = 0 \quad (1-10)$$

$$\begin{array}{l} \text{(Organic Matter)} \end{array} \quad \frac{-W \partial G}{\partial x} - KG = 0 \quad (1-11)$$



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C=concentration of sulphate

G=concentration of organic matter (moles/unit mass of sediment)

K=First order rate constant.

L=Stoichometric coefficient, moles of sulphate reduced/moles of organic matter oxidised to  $\text{CO}_2$  normally taken as 0.5

$F = \frac{(1+\phi)\rho}{\phi}$  and is the concentration conversion factor where  $\phi$  is the porosity and  $\rho$  is the density of the sediment.

$D_s$  is the sediment diffusivity

These equations have been solved for the boundary conditions:

$$X=0, \quad C=C_0, \quad G=G_0$$

and

$$X \rightarrow \infty, \quad C=C_\infty, \quad G \rightarrow 0$$

The value of  $C_\infty$  used in the calculations may be  $<0$  if sulphate is limiting and is selected to give the best fit to the true sulphate profile in the sediment.

$$C = \frac{W^2 \cdot F \cdot L \cdot G_0}{W^2 + K \cdot D_s} \exp[(-K/W)X] + C_\infty \quad (1-12)$$

$$G = G_0 \cdot \exp[(-K/W)X] \quad (1-13)$$

and

$$C_0 - C_\infty = \frac{W^2 \cdot F \cdot L \cdot G_0}{W^2 + K \cdot D_s} \quad (1-14)$$

The model predicts an exponential decrease of sulphate and organic carbon with depth.  $G_0$  represents the

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metabolisable fraction of organic matter. As seen above  $K$  varies depending on the type of organic matter present, which is related via the Toth and Lerman equation to the rate of sedimentation. Fig (8) shows the pore water sulphate profile of the Santa Barbara Basin (Data from Goldhaber and Kaplan 1963) and the best fit curve from equation 12 with  $C_0 = 27 \mu\text{moles/cc}$ ,  $C_\infty = 8 \mu\text{moles/cc}$  and  $K/W = 0.015 \text{ /cm}$ . The positive value for  $C_\infty$  indicate a limitation of sulphate reduction by organic matter. Fig (9) shows the pore water sulphate profile for a core from the Carmen Basin (Goldhaber and Kaplan 1980) in this case sulphate is limiting and goes to zero at about 2m.

By summing the total amount of sulphate reduced and assuming that there is sufficient iron present to trap sulphide produced it is possible to calculate the amount of iron sulphide added to the sediment in the zone of diffusion. Berner (1980) showed the equations to be;

$$\Sigma S = \int_0^x (R_{SO_4}/W) dx \quad (1-15)$$

$R_{SO_4}$  = Rate of reduction of sulphate

according to the model

$$R_{SO_4} = LFKG \quad (1-16)$$

$$\Sigma S = LFG_0[1 - \exp(-K/W)X] \quad (1-17)$$

These equation may be taken further and it is possible to examine the factors that affect the total amount of

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pyrite formed in the zone of diffusion. If sulphate is considered to be limiting then  $C=0$  at some depth  $X$ , therefore from eq. 11

$$0 = \frac{[W^2 F.L.Go]}{[W^2 + K.Ds]} \exp[-(K/W)X] + C_{\infty} \quad (1-18)$$

Substituting for  $C_{\infty}$  from I-5 and solving for  $X$

$$X = \frac{W}{K} \log_e \{1 - [(W^2 + K.Ds) / (W^2 F.L.Go)]X\} \quad (1-19)$$

Also solving for  $\Sigma S$

$$\Sigma S = [Co(W^2 + K.Ds) / W^2] \quad (1-20)$$

From Toth and Lerman  $K = AW^2$

Therefore

$$\Sigma S = Co(1 + A.Ds) \quad (1-21)$$

and

$$X = -(1/AW) \cdot \log_e \{1 - Co \cdot (1 + A.Ds) / (FLGo)\} \quad (1-22)$$

From equations 21 and 22 we see that the total amount of iron sulphide formed in the zone of diffusion is independent of the initial concentration of metabolisable organic matter, and is only dependent on the diffusivity of the sediment and the concentration of sulphate in seawater. The depth to the base of the sulphate reduction zone is inversely proportional to the rate of sedimentation and dependent on a function of  $Go$  such that as  $Go$  increases  $X$  decreases. Assuming some general values for the parameters in 21 the approximate quantity of pyrite sulphur precipitated in the zone of diffusion may be calculated.

$$A = 0.04 \text{ yr/cm}^2, \quad Ds = 100 \text{ cm}^2/\text{yr}, \quad Co = 28 \mu\text{moles/ml}$$

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Hence  $\Sigma S = 140$  moles/ml or approx 0.6% sulphur. We may also calculate the minimum value of  $G_o$  which will result in sulphate limitation. This will occur when sulphate goes to zero at  $X =$  hence from equation 22.

$$\frac{1 - C_o(1 + A \cdot D_s)}{L \cdot F \cdot G_o} = 0 \quad (1-23)$$

From the values above  $G_o = 350 \mu\text{moles/g} = \text{approx } 0.4\% \text{ C}$ . Below this value organic carbon will be limiting in sulphate reduction and the resulting sulphide concentrations will be  $< 140 \mu\text{moles/ml}$  porewater and proportional to the initial concentration of metabolisable organic matter ( $G_o$ ). From the Santa Barbara Basin data the value for total reduced sulphide is  $130 \mu\text{moles/ml}$  in agreement with the organic carbon limitation of sulphate reduction. Work of Goldhaber and Kaplan (1980) on the Pascadero Basin found  $\Sigma S$  to be 0.55% well in agreement with the above figures.

The total amount of pyrite formed will depend on the availability of iron to fix the reduced sulphide. If insufficient iron is present hydrogen sulphide may diffuse up through the sediment to be reoxidized in the surface layers. If though we assume complete trapping by iron, the total amount of pyrite will be the sum of that formed in the zone of bioturbation and that in the zone of diffusion. As seen above the amount of pyrite formed

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in the zone of diffusion has an upper limit imposed by the diffusion of sulphate. It may be considered that variation in the total amount of sulphate reduction occurring is dependent on the extent of organic metabolism in the zone of bioturbation. When metabolism is extensive the organic matter surviving the zone is insufficient to satisfy totally sulphate diffusion. When the metabolism is restricted sulphate reduction is limited by diffusion. As seen above the amount of pyrite formed in the zone of bioturbation is a complex interaction of reductions and oxidations, such that the sediment which undergoes the greatest extent of sulphate reduction need not be the one that contains the most pyrite. Limitation of the residence time of the sediment in the zone of bioturbation, eg. by increased sedimentation rate, will lead to the greater preservation of organic matter through the sulphate reduction and into deeper zones (cf Curtis, 1977).

### 5.2 Sulphate Reduction in Sediments From Anoxic Environments

There are two distinct differences between the of sulphate reduction in sediments from oxic and anoxic environments.

1. Lack of bioturbation leads to the top of the zone of diffusion lying within a few millimetres of the sediment



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water interface.

2. Sulphate reduction takes place in the anoxic water column.

The sulphate reduction in the zone of diffusion follows the same pattern as in the oxic environment and the same limitations apply. Sulphate reduction in the water column is best illustrated by example.

The best example of a present day environment in which sulphate reduction occurs in the water column is the Black Sea. The conditions occur from the sea floor (about 2200m) to within 200m of the surface. The data of Sorokin (1962) indicate that the majority of sulphate reduction occurs at the oxic/anoxic boundary and that further reduction takes place at the sediment water interface (Table 3). The anoxic water column limits the aerobic oxidation of organic matter prior to the entry into the sulphate reduction zone. The more metabolisable fraction is therefore better preserved and a larger proportion of organic matter is available for sulphate reduction. The majority of pyrite formation takes place at the sediment water interface by the reaction of the dissolved hydrogen sulphide with iron containing minerals. Berner (1970) considers that in such instances the main limitation of pyrite formation is reactive iron.

Rees (1973) suggested that the bacterial population in the Black Sea water column had grown to such a size

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that it utilized all organic matter as it was supplied. If such is the case, further sulphate reduction in the zone of diffusion (the sediment) will be limited by the lack of organic matter. It is possible to envisage conditions where the extent of anoxic water and anaerobic metabolism are less and sufficient organic matter for limitation of sulphate reduction by sulphate diffusion to occur. In such a case the sedimentation rate will play a part in preserving organic matter beyond the sulphate reduction zone, by limiting the extent of sulphate reduction occurring at the sediment surface where the sulphate supply is essentially unlimited.

### 5.3 Relationship Between Pyrite Sulphur and Organic Carbon

As organic matter is combusted during sulphate reduction it is reasonable to consider that some quantitative relationship exists between reduced sulphur and organic carbon. Berner (1970) found a linear relationship between the %S pyrite and %C organic in the surface two centimetres of the Connecticut coastal sediments. Sweeney (1972) and Goldhaber and Kaplan (1974) expressed the relationship as,

$$C_m = \frac{3S_m (1/K - 1)}{4 (1 - X)} \quad (1-24)$$

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where  $C_m$  = the measure % organic carbon  
 $S_m$  = the % reduced sulphur in the sediment  
 $X$  = Fraction of sulphide reoxidized  
 $K$  = Fraction of deposited organic matter  
oxidized during sulphate reduction.

From a compilation of data from recent sediments Sweeney (1972) found the mean S/C ratio for recent sediments to be 0.36 ( $C/S = 2.8$ ) but with a large scatter (Fig 10). The scatter is interpreted as resulting from the following sources.

1. Sulphur and organic carbon values were not measured on the same core samples.
2. To fall on the same line  $K$  would have to be identical for all sediments. This is unreasonable and hence data from individual environments show less scatter.
3. Sulphate reduction continues in the pore water of the zone of diffusion (as described above) and this can cause deviation from the line.
4. The extent of  $X$  may vary between environments or with depth in a single sediment.

All the data for the study were derived from sediments deposited in oxic bottom water. It is assumed by Goldhaber and Kaplan that the the majority of sulphate reduction occurs in the top few centimetres of the sediment. This corresponds with the model of sulphate reduction given above where a maximum about 0.5% S is

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deposited in the zone of diffusion. As seen above the value of  $X$  may vary considerably upto 0.6 (60% reoxidation) (Aller 1977). It is surprising that such a wide range of possible  $X$  values is not reflected in the  $C$  vs  $S$  plots. The reason may be that both  $K$  and  $X$  are related to the residence time in the zone of bioturbation and hence an increased  $K$  is associated with an increased  $X$  and the effect of one is cancelled by the effect of the other.

Leventhal (1983) examined the  $S/C$  ratios in the Black Sea, and found two distinct differences from the those described by Sweeney, 1. The average  $C/S$  ratios were lower. 2. Linear least squares regression lines had positive intercepts on the  $S$  axis.

The two characteristics result from the great extent of anoxic water and the occurrence of sulphate reduction in that water column. The limited extent of oxic water in the Black Sea results in a larger proportion of metabolisable organic matter entering the zone of sulphate reduction and so  $K$  in eq. 1-24 is larger. The reduction of sulphate in the water column gives rise to the formation of pyrite before burial. As the hydrogen sulphide in the water column is mobile the pyrite formed becomes decoupled from its complementary organic matter and the positive intercepts on the  $S$  axis result. Berner and Raiswell (1983) suggest that the lower  $C/S$  ratios of euxinic sediments can be used to distinguish them from

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normal marine sediments.

In both the normal and, especially, the euxinic conditions the availability of iron may play an important role in the final C/S ratio, as the final pyrite content depends not only on the supplies of sulphate and organic carbon but also on the presence of iron to trap the sulphide formed. A lack of iron will lead to a lower than expected reduced sulphur content and hence an apparently higher C/S ratio.

### 6 Sulphur Isotopic Composition Of Pyrite.

As seen above the bacterial reduction of sulphate produces significant fractionations in sulphur isotopes. In table 4 below (Chambers and Trudinger 1979) is given a list of the apparent fractionation factors for a variety of waters and sediments. These fractionations are of the order of or greater than the maximum fractionation (-46‰) achieved in laboratory experiments. Rees (1973) explained fractionations of -50‰ in terms of the operating conditions of the bacteria, but as seen above doubt has been cast on the fractionation adopted by Rees. The larger fractionations could be explained by the reversibility of the bacterial pathway (Trudinger and Chambers 1973) but this would only occur at very slow rates of reduction when organic concentrations are low, and is not experimentally



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substantiated. A second explanation for the large fractionations is the recycling of sulphide by either chemical or bacterial reoxidation. Such reoxidation has been seen to occur in sediments of Long Island Sound (Goldhaber et al 1977). Nakai and Jensen (1964) indicate that sulphide reoxidation occurs with very little fractionation in the sulphur isotopes. Reoxidized sulphide may potentially act as a source of isotopically light sulphate. It is not known though whether the light reoxidized sulphide may build up to a great enough concentration to affect noticeably the apparent fractionation. If reoxidation does occur in the sediment the sulphate in the pore water may become isotopically lighter than seawater and hence the apparent fractionations for sediments in Table 4, which are calculated relative to seawater, appear too great. This may also explain why the mean and extreme fractionations given for sulphate reduction occurring in water columns are generally less than those for sediments. Data from the Carmen Basin in the Gulf of California (Goldhaber and Kaplan 1980) show excess and isotopically light sulphate in the surface (20 to 30cm) which Goldhaber and Kaplan suggested might be due to sulphide reoxidation but did not know whether this was due to extraction and handling of the core. The data of Vinogradov et al (1962) for the Black Sea show that although the fractionation factor is fairly constant sulphate from

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the oxygen/hydrogen sulphide transition zone shows marginally lighter  $\delta^{34}\text{S}$  values. Evidence of light sulphate in older sediments comes from the work of Benmore et al (1983) on the sulphur isotopic composition of sulphate in francolite. The sulphate showed depletion in  $^{34}\text{S}$  of up to 10‰ compared to seawater sulphate. These francolites are thought to form at the oxic/anoxic boundary in the sediment where sulphide reoxidation occurs and the pH is lowered promoting the precipitation of francolite.

Goldhaber and Kaplan (1975) suggested that, as in laboratory experiments, there exists a relationship between the log. rate of sulphate reduction and the fractionation (fig 11). The rates of sulphate reduction quoted in laboratory experiments are per cell, and thus would imply that marine sediments contain a constant bacterial population. Chambers and Trudinger (1979) point out that this conclusion is not supported by counts of bacterial population. The relationship between rate of reduction and fractionation together with the Toth and Lerman (1977) relationship (eq 1-9 above) has been used by Maynard (1980) to calculate relative rates of sedimentation in shale of the Devonian and Carboniferous of the U.S.A. In the case of ancient sediment the isotopic displacement between the pyrite and the average  $\delta^{34}\text{S}$  value of the contemporary seawater does not represent the fractionation factor.

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Pyrite, as seen above, does not form totally in the surface layers of the sediment where the isotopic displacement

represents something approaching the true fractionation. Pyrite is also formed in deeper zones of the sediment where sulphate is supplied by diffusion and consequently the sulphate reservoir is not essentially infinite. The removal of light sulphide causes an enrichment in the sulphate which is reflected in the subsequent formation of of sulphide. The enrichment of sulphate follows a Rayleigh equation,

$$R_t = R_o \cdot F^{(1-1/\alpha)} \quad (1-25)$$

and the corresponding equation for the sulphide is

$$\frac{P_t}{R_o} = \frac{1-F}{1-F}^{(1/\alpha)} \quad (1-26)$$

where F is the fraction of sulphate remaining and  $\alpha$  is the fractionation factor  $R_o$ ,  $R_t$ , and  $P_t$  are respectively the isotopic ratio  $^{34}\text{S}/^{32}\text{S}$  for the original sulphate and the final sulphate and sulphide. These variations are shown in data on the Baltic Fig (12) (Hartmann and Nielsen 1969) These equations show that at total reduction the final product must have the isotopic composition of the initial sulphate. Goldhaber and Kaplan (1980) have demonstrated that as the sediment is

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not a totally closed system but sulphate is supplied by diffusion, the preferential removal of  $^{32}\text{S}$  enhances the diffusion gradient of  $^{32}\text{S}$  relative to  $^{34}\text{S}$  so that the final isotopic composition is lighter than expected from the Rayleigh equation. Goldhaber and Kaplan calculated that, on complete reduction of sulphate, the resulting sulphide should be displaced from seawater by some -25‰, assuming a fractionation of -45‰.

When considering the final isotopic composition of pyrite in ancient sediment the proportions formed in open system (anaerobic water column or bioturbated sediment) and in the partially closed zone of diffusion must be determined. Fine grained disseminated pyrite should show a mix representing the general diagenetic pattern of the sediment. Concretions and shell replacements may show highly biased isotopic compositions due to the preferential formation of pyrite in one or other of the zones or due to their acting as separate closed or partially closed systems within the sediment. In many cases pyrite concretions and shell infillings tend to possess more positive isotopic compositions compared to the fine grained pyrite. This is shown by data on Jet Rock concretions (Coleman and Raiswell 1981) and from various Jurassic shales studied by Hudson (1982).

### 7. Conclusions.



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1. Sulphate reduction is one of a series of diagenetic reactions involving the combustion of organic matter.
2. It occurs after the consumption of oxygen as sulphate reducing bacteria are obligate anaerobes.
3. Sulphate reducing bacteria have a wide tolerance of physical conditions are found in almost all natural environments in which oxygen is not present.
4. The sulphur isotopic fractionation is directly related to the specific rate of bacterial sulphate reduction, which is affected by several factors but most importantly the concentration and composition of the organic substrate. Where sulphate is not limiting in sulphate reduction the fractionation is found to vary between -9 and -46‰. When sulphate is limited (<2mmoler) the fractionation may be as small as +3‰. This range of fractionations is not completely understood by the microbiologists.
5. One consequence of the reduction of sulphate is the formation of pyrite. This occurs via the formation of various intermediary iron sulphides such as mackinawite and greigite. The pathway of formation can result in distinct morphologies, particularly that of framboids when greigite is an intermediary.
6. The sulphate reduction zone in the sediment can be divided into two parts a) a zone where bacteria are directly in contact with the large seawater sulphate reservoir b) A zone where sulphate is supplied by



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diffusion. The former may occur either in the anoxic seawater or in the zone of bioturbation where the overlying seawater is mixed with the sediment by the action of macro-organisms. In the latter case the maximum amount of sulphate reduced is limited by the sulphate supply.

7. A relationship exists between the total reduced sulphide, measured as pyrite sulphur, in a sediment and its organic carbon concentration. In normal marine shales, where bottom water are oxic, a C/S ratio of about 3 is found. In euxinic conditions the C/S ratio are smaller. Both of these values may be altered if iron becomes limiting and not all reduced sulphide is trapped as pyrite.

8. Isotopic fractionations found in sediments are generally greater than those found in laboratory experiments, averaging about -5‰ in sediments and -43‰ in anoxic waters. This suggests that sulphate-reducing bacteria function at a lower specific rate of reduction than is normally found in experimental conditions. Some of the larger fractionations may result from the incorporation of isotopically light sulphate produced by the reoxidation of sulphide. Hence in open system conditions pyrite forms with an isotopic composition of <seawater-45‰

9. Isotopically heavy sulphur is added within the zone of diffusion. The enrichment follows the Rayleigh

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fractionation equation but is modified by the effects of diffusion so that the resulting sulphide is lighter and on total reduction of sulphate has a composition of about seawater-25‰.

10. The final isotopic composition of the pyrite depends on the proportion of pyrite formed in the open system and the partially closed conditions, the total amount formed depending on the relative availability of iron , sulphate and organic matter. Pyrite associated with concretions and shells may show markedly different isotopic composition to the general dispersed pyrite in the sediment due to the distinct environment or micro-environment they represent.

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- Fig.5. Summary of pyrite formation in the upper layers of marine sediments. The pathway indicates the intermediates which lead to pyrite framboids and single crystal formation. (Goldhaber and Kaplan 1974)
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- Fig.11 Log. rate of sulphate reduction against  $\delta^{34}\text{S}$  initial sulphide. 1. Various laboratory experiments using pure cultures. 2. Nakai and Jensen (1964). 3. Naria Del Ray Harbour, isotope data Sweeney (1977) rate Goldhaber

and Kaplan (1975). 4. Pettaquamscott River Basin, Rhode Island, Orr and Gaines (1974). 5. Newport marsh South California. Isotope data Kaplan et al (1963) rate calculated from Emery (1960). 6. Santa Barbara Basin . Isotope data Sweeney (1972) ,Rate Berner (1972). 7. Carmen Basin Gulf Of California data Goldhaber (1974). 8&9 Pascadero Basin Gulf of California data as 7. 10. Santa Catalina Basin South California Data as 5. 11. East Cortez Basin South California, isotope data Sweeney (1972) rate calculated from Emery (1960). 12. Long Basin California data as 5.

Fig 12.  $\delta^{34}\text{S}$  variation (left) and increase of S concentration (right) with depth from modern marine sediment from the Baltic Sea of Kiel (Hartmann and Nielsen 1969)



Table 1  
Depth Sequence of Diagenetic Zones

Zone (depth)	Organic Degradation reactions		
Zone 1 Aerobic Oxidation (mm-cm)	$\text{CH}_2\text{O} + \text{O}_2 \longrightarrow \text{H}^+ + \text{HCO}_3^- \quad \Delta G_o = -475 \text{kJ/mol}$		
Post Oxidic Zone	$5\text{CH}_2\text{O} + 4\text{NO}_3^- \longrightarrow 2\text{N}_2 + 4\text{HCO}_3^- + 3\text{H}_2\text{O} \quad \Delta G_o = -448$ $(\text{CH}_2\text{O} + 3\text{CO}_2 + \text{H}_2\text{O} + 2\text{MnO}_2 \longrightarrow 2\text{Mn}^{2+} + 4\text{HCO}_3^- \quad \Delta G_o = -349)$ $(\text{CH}_2\text{O} + 7\text{CO}_2 + 4\text{Fe}(\text{OH})_2 \longrightarrow 4\text{Fe}^{2+} + 8\text{HCO}_3^- + 3\text{H}_2\text{O} \quad \Delta G_o = -114)$		
Zone 2 Sulphate Reduction (1-10m)	$2\text{CH}_2\text{O} + \text{SO}_4^{2-} \longrightarrow 2\text{HCO}_3^- + \text{HS}^- + \text{H}^+ \quad \Delta G_o = -77$		
Zone 3 Fermentation to uncertain depth	$2\text{CH}_2\text{O} \longrightarrow \text{CH}_4 + \text{CO}_2 \quad \Delta G_o = -58$		
Deeper Zones	abiogenic reactions, decarboxylation, dehydration, thermal cracking.		

Table 2  
Summary Of Laboratory Synthesis of Pyrite by Various  
Workers (from Goldhaber & Kaplan 1974)

Reactants	pH	Time (days)	Temp (°C)	Products	Ref.
$\text{Fe}^{2+} + \text{H}_2\text{S} + \text{S}^0$	Alkaline	7	100	$\text{FeS}_2$	1
$\text{FeS} + \text{S}^0$	4.5	7	22	$\text{FeS}$ , No $\text{FeS}_2$	2
$\text{FeS} + \text{S}^0 + \text{O}_2$	5.5	36	25	$\text{FeS} + \text{S}^0$	2
$\text{FeS} + \text{Na}_2\text{S}_x$	6.9-7.9	77	65	$\text{FeS}$ , No $\text{FeS}_2$	1
$\text{FeS} + \text{S}^0 + \text{Na}_2\text{S}_x$	6.9-7.9	14	65	$\text{FeS}_2$	1
$\text{FeS} + \text{Na}_2\text{S}_x$	7	7	25	$\text{FeS}_2 (\text{S}^0)$	3
$\text{FeS} + \text{S}^0$		7	68-85	$\text{FeS}_2$	4
$\text{FeSO}_4 + \text{H}_2\text{S} + \text{O}_2$	3	15Min	85-90	$\text{Fe}_3\text{S}_4$ , $\text{FeS}_2$	5
$\text{FeSO}_4 + \text{H}_2\text{S} + \text{O}_2$	3	2	60-65	$\text{FeS}_2$	5
$\text{FeSO}_4 + \text{H}_2\text{S} + \text{O}_2$	3	25	40	$\text{FeS}_2$	5
$\text{FeOOH} + \text{H}_2\text{S}$	4	14hrs	20-25	$\text{FeS}_2$ , $\text{FeS}$	5
$\text{FeOOH} + \text{H}_2\text{S}$	4.4-7.0	7	25	$\text{FeS}_2 (\text{FeS})$	3
$\text{FeOOH} + \text{H}_2\text{S}$	3.8-6.5	24hrs	25	$\text{FeS}_2$	2

Minor product in Parentheses

$\text{FeS}$  indicates acid volatile sulphide.

References. 1 Berner 1970. 2 Roberts et al 1972. 3 Rickard 1974. 4 Sweeney 1972. 5 Berner 1964.

Table 3

Sulphate Reduction and Isotope Fractionation In the Waters of the Black Sea. (Station 4751 sulphate reduction data from Sorokin (1962), isotope data from Vinogradov et al (1962).

Depth (m)	Sulphate Reduction ( $\mu\text{mol/m /day}$ )	Fractionation $\Delta^{34}\text{S}$ (Sulphide-sulphate)
180	0	—
200	—	-52.4
215	200	--
270	65	--
300	--	-52.6
400	24	--
500	0	-54.6
1000	0	-52.2
2200	0	-50.3
Benthic		
Waters	16	—

Table 4

Apparent Fractionations Factors for Reduction in Marine and Inland Waters and Sediments (from Chambers & Trudinger 1979)

Locality	Ref.	Fractionation $\alpha$ Waters      Sediments
Dead Sea	1	
(Ein Gedi)		1.036
(Masada)		1.035
Sea Of Cortez	2	
Site 663		1.046
664		1.055
665		1.044
667		1.048
Pacific Ocean	2	
(off Mexico)		
Site 668		1.047
669		1.059
672		1.057

Locality	Ref.	Fractionation $\alpha$	
		Waters	Sediments
(Near Hawaii)			
site 681			1.052
Black Sea	3		
Site 4740		1.047	1.053
4751		1.052	1.041
4745		1.054	1.052
4754		1.054	1.048
4752			1.048
4759			1.052
4753			1.050
Santa Barbara			
Basin	4		1.047
Santa Monica			
Basin	4		1.034
Santa Catalina			
Basin	4		1.050
San Diego			
Trough	4	1.017-1.062	
Newport Marsh	4	1.035-1.040	
Long Island Sound			
Connecticut	5		1.034
Brandford Bay			
Connecticut	5		1.042
Lake Veisove			
U.S.S.R.	6	1.021	
Lake Sakavo			
U.S.S.R.	6	1.028	
Green Lake, N.Y.	7	1.055	
Ace Lake			
Antarctica	8	1.052	
Spring Waters			
Various From			
N.W.T. Canada	9	1.035-1.048	
Lake Mogil'noe			
U.S.S.R.	10	1.045	

References. 1 Nissenbaum & Kaplan (1972). 2 Lein et al (1976). 3 Vinogradov et al (1962). 4 Kaplan et al (1963). 5 Nakai & Jensen (1964). 6 Matrosov et al (1975). 7 Deevey et al (1963). 8 Burton and Barker (in press). 9 Van Eurdin & Krouse (1978). 10 Ivanov et al (1976).

Fig.1    Effect of rate of burial on oil prospect  
          (Coleman et al 1979)



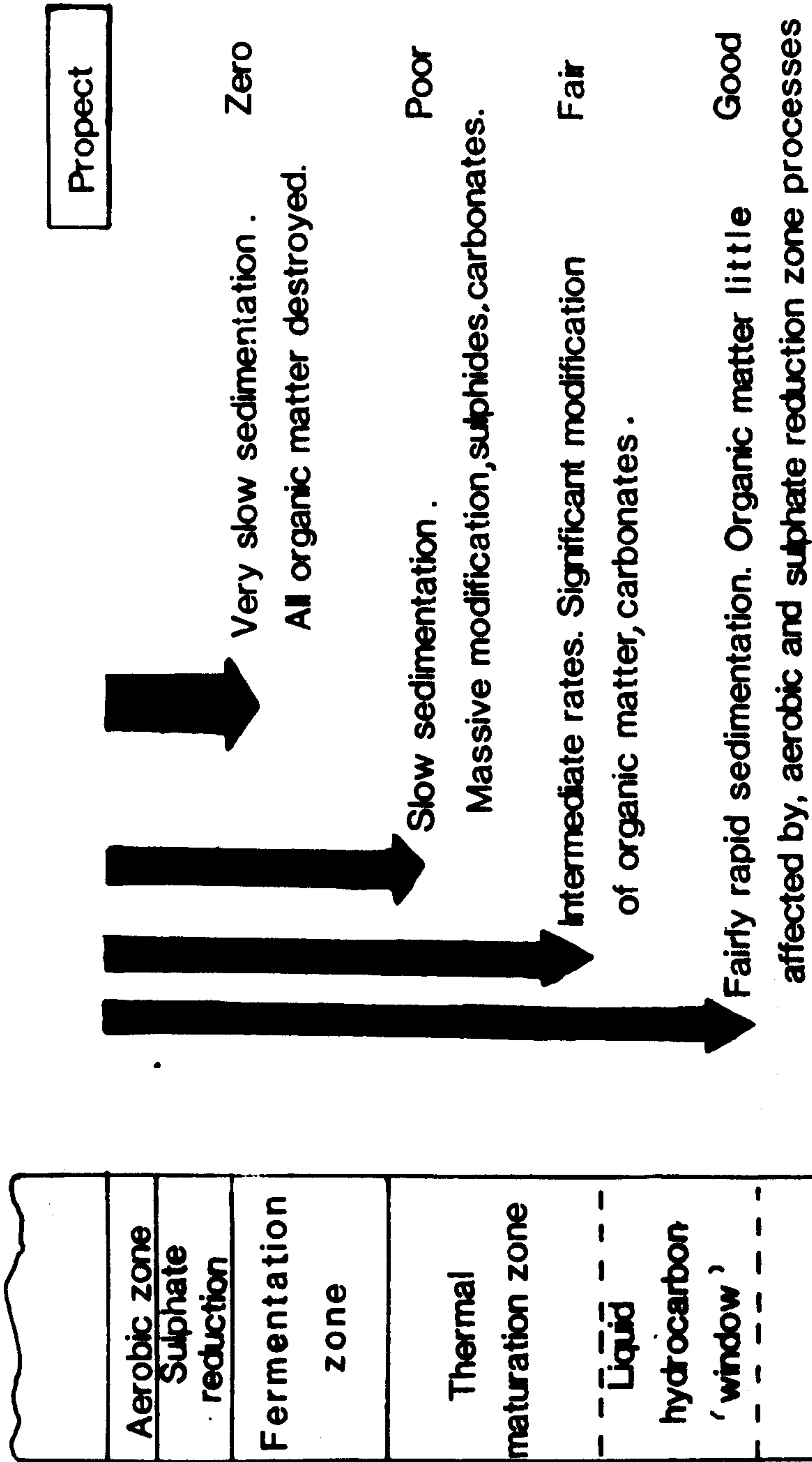


Fig.2 Plot of fractionation factor  $\delta^{34}\text{S}$  Vs Specific  
rate of bacterial sulphate reduction for  
organic substrates (Chambers & Trudinger 1979)

fig2

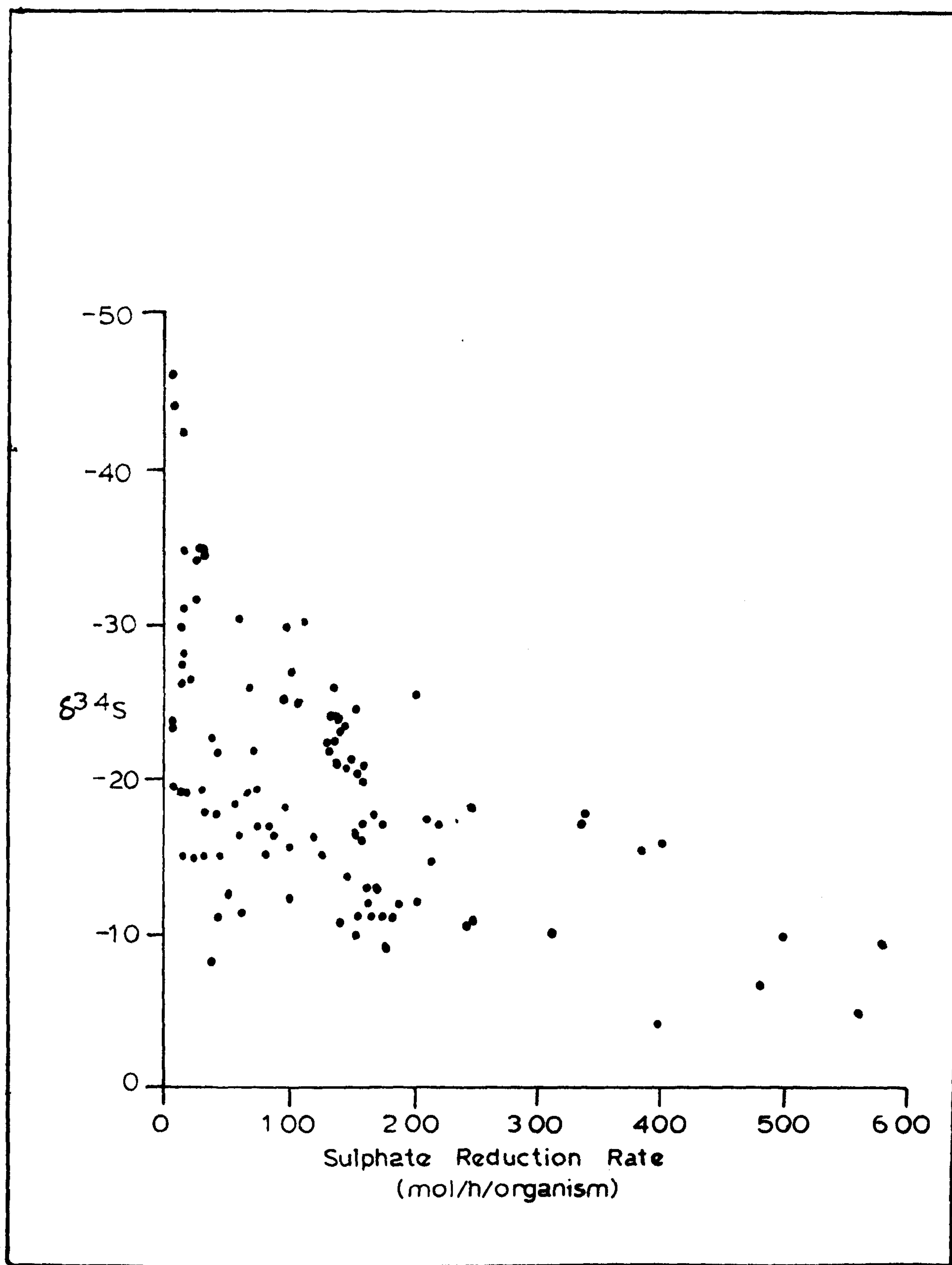


Fig.4 Stability of various iron minerals on an Eh pS Diagram (Berner 1971).  $\text{pH}=7.37$   $\text{Log } \text{PCO}_2 = -2.40$   
 $T=25^\circ\text{C}$   $\text{P}_{\text{total}}=1$  atm. Field marked H corresponds to the area where water is unstable relative to  $\text{H}_2$  gas. measurements in natural sediments fall close to the dashed line.

Fig.7 A Log-Log plot of K(the rate constant for sulphate reduction) vs W(Rate of sedimentation) for marine sediments from Berner 1980. (Modified from Toth and Lerman 1977 with additional data from Berner 1978)

fig 4

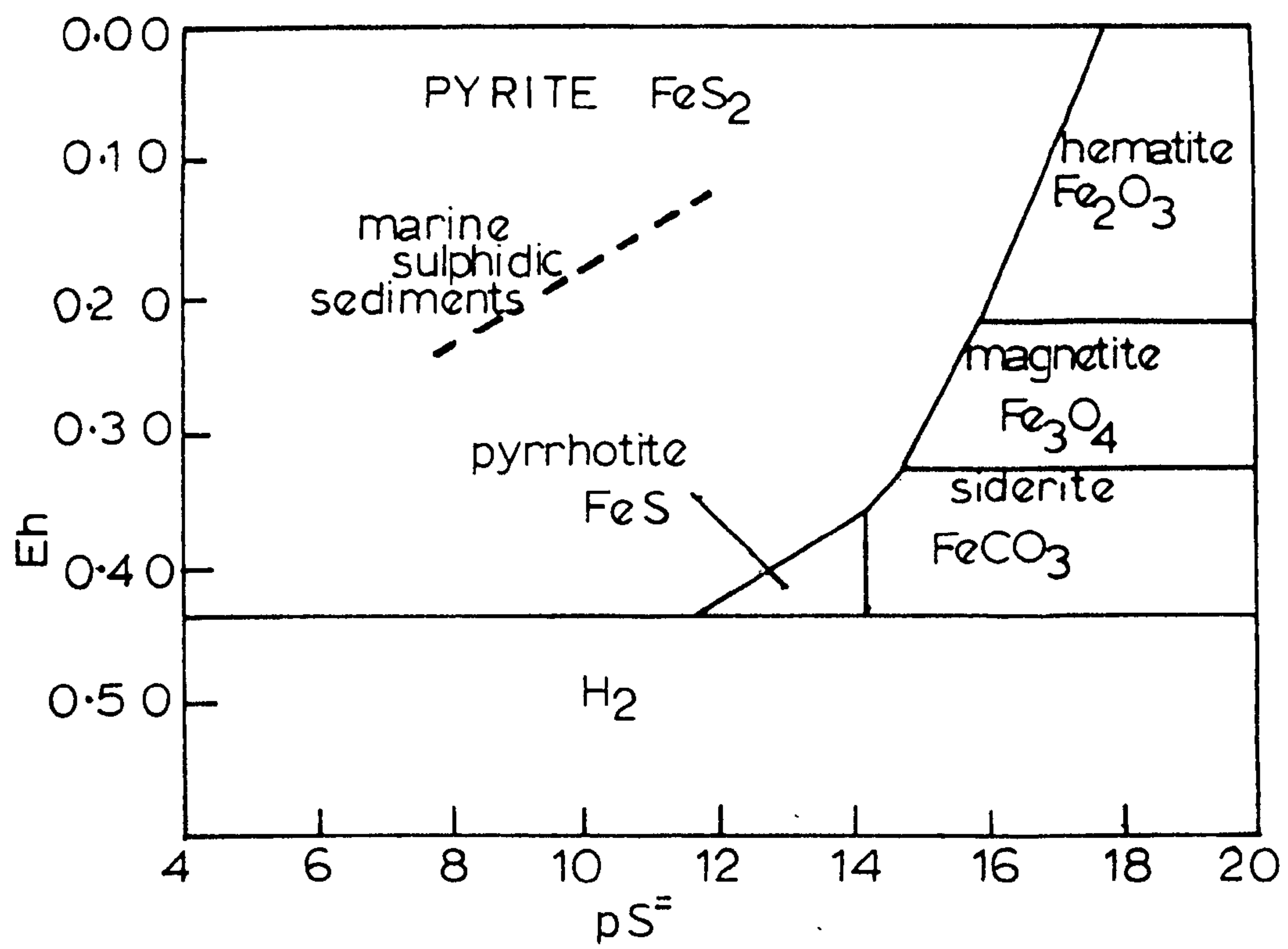
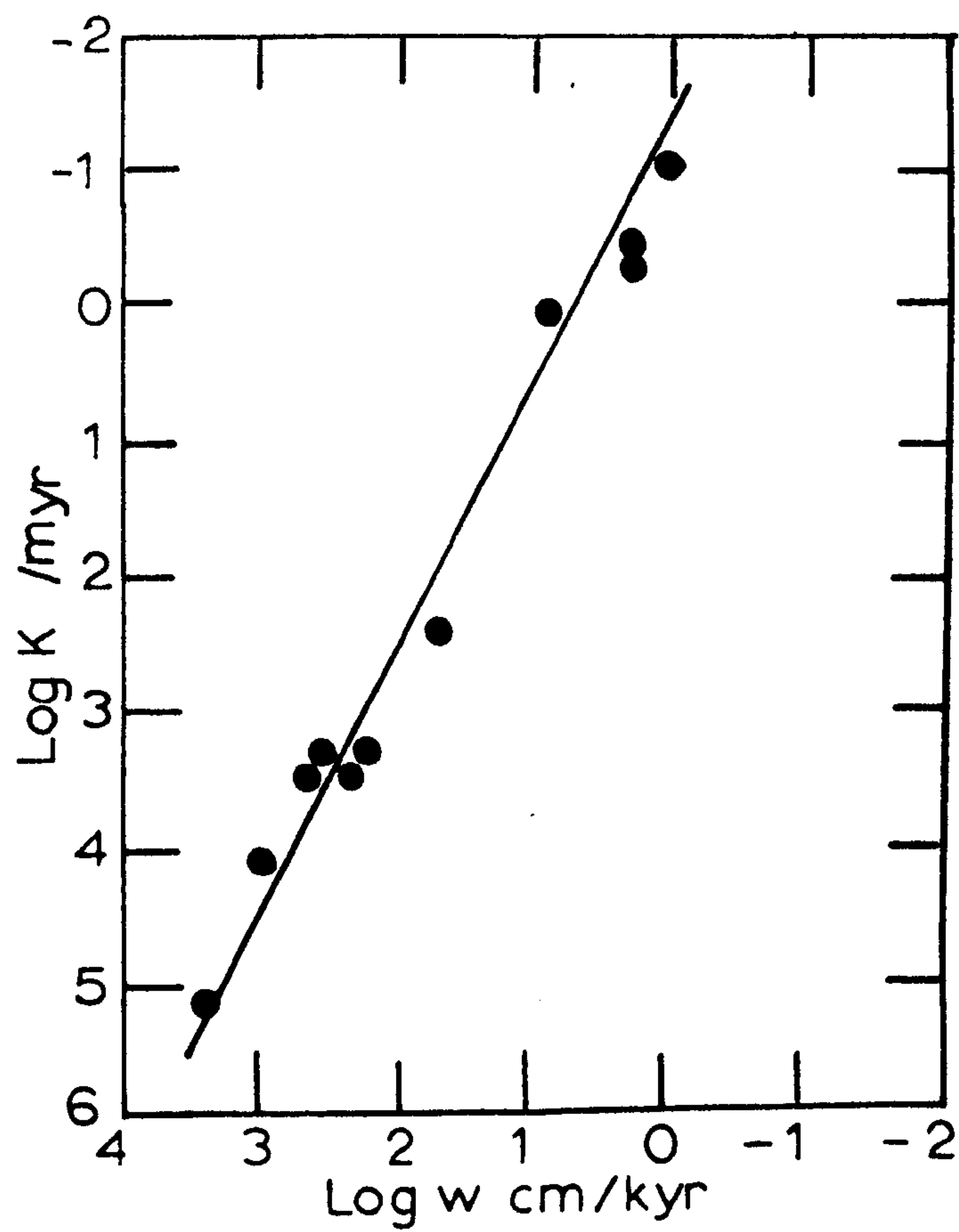


fig 7





**Fig.5. Summary of pyrite formation in the upper layers  
of marine sediments. The pathway indicates the  
intermediates which lead to pyrite framboids  
and single crystal formation. (Goldhaber and**

**Kaplan 1974)**

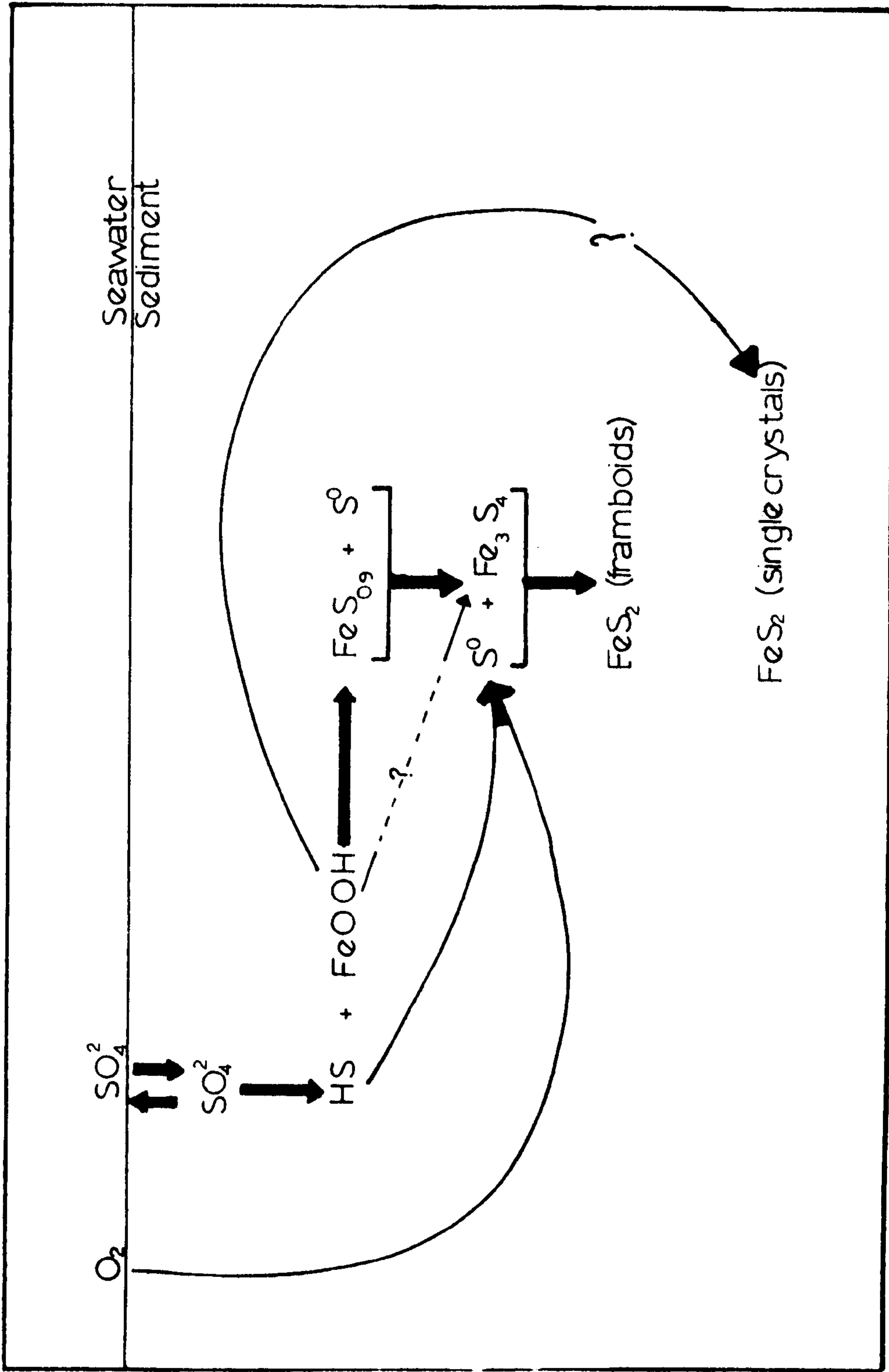


fig 5

**Fig.6**    A schematic representation of the  
intermediaries involved in the formation of  
pyrite framboids. (Goldhaber and Kaplan 1974)

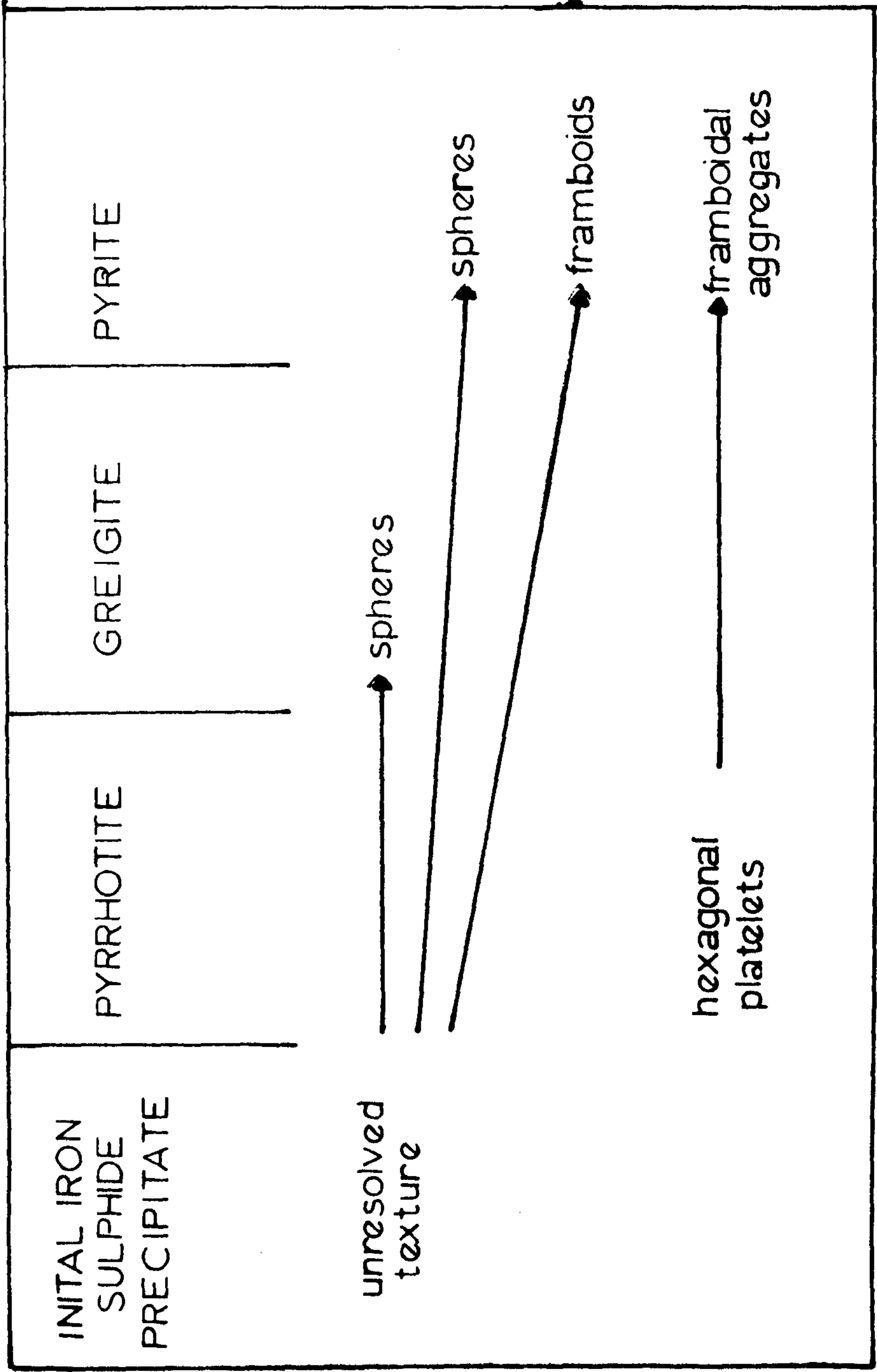


fig 6

Fig.8a Pore water sulphate profile for sediments from  
the Santa Barbara Basin (Kaplan et al 1963)

Fig.8b. Pore water sulphate profile for sediments from  
the Carmen Basin Gulf of California (Goldhaber  
and Kaplan 1980)



fig 8

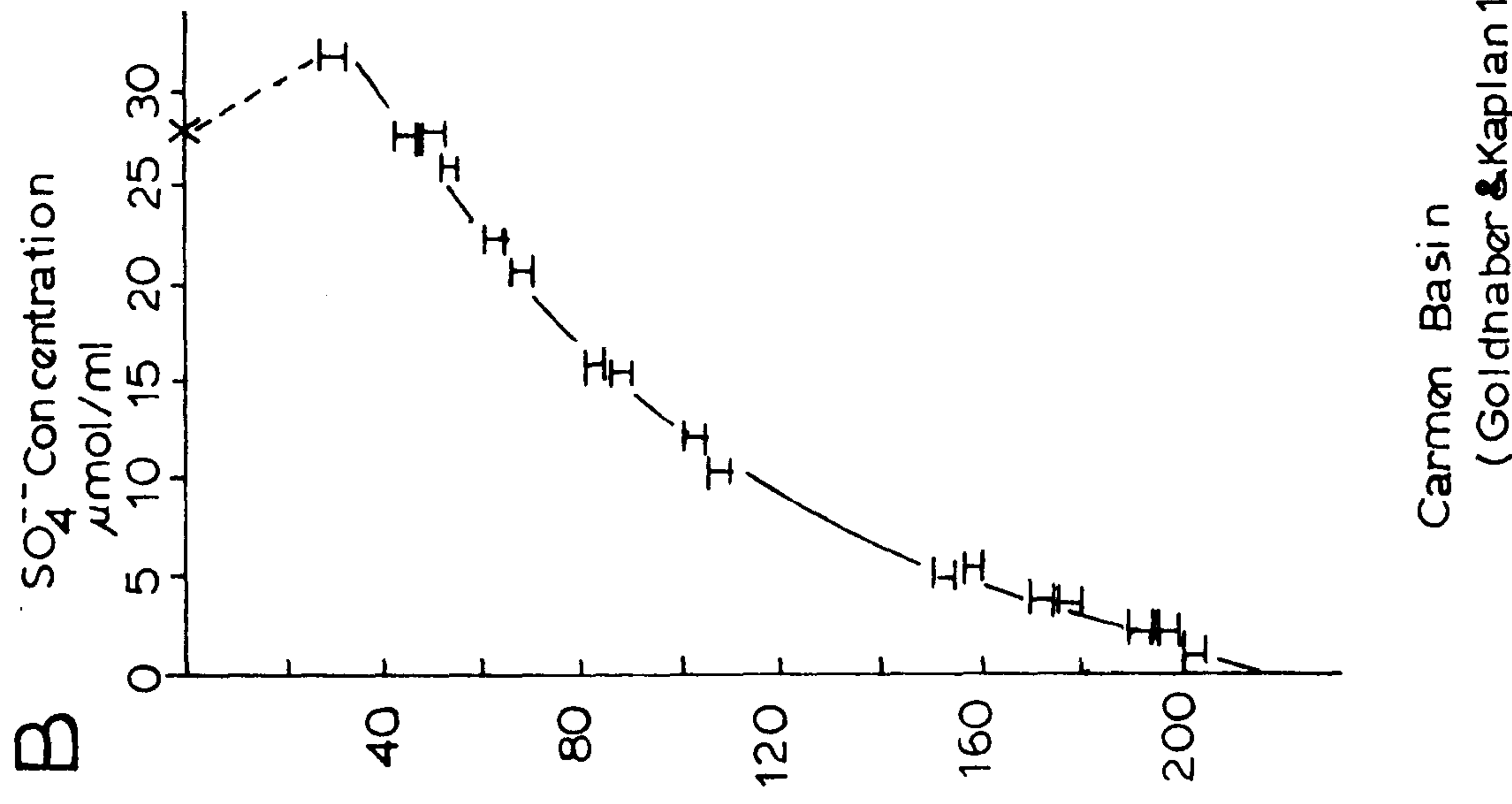
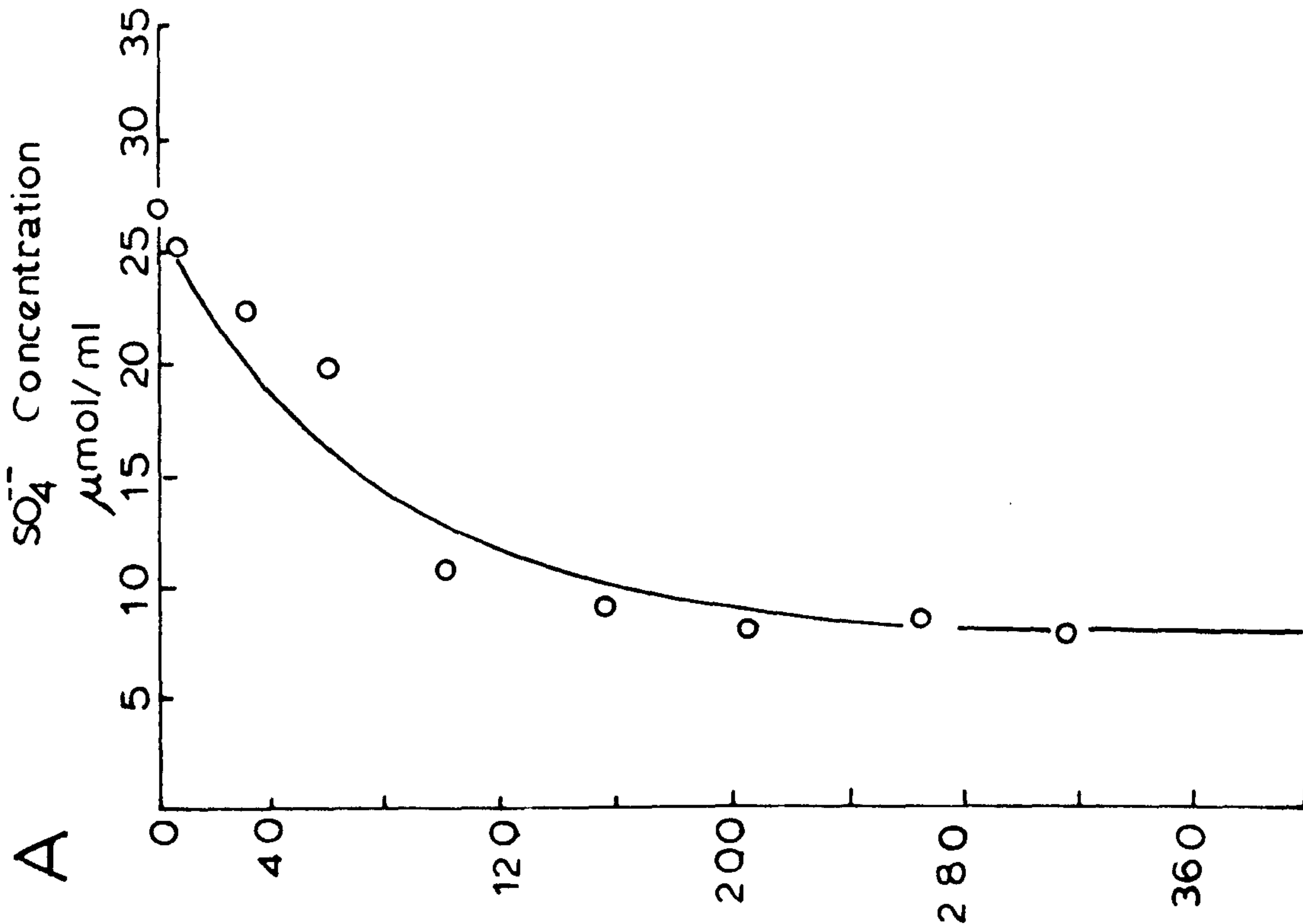


Fig.10 sulphide and organic carbon measurements from  
the solid fraction of different depths in  
sediment from recent marine environments.  
(Goldhaber and Kaplan 1974)

fig 10

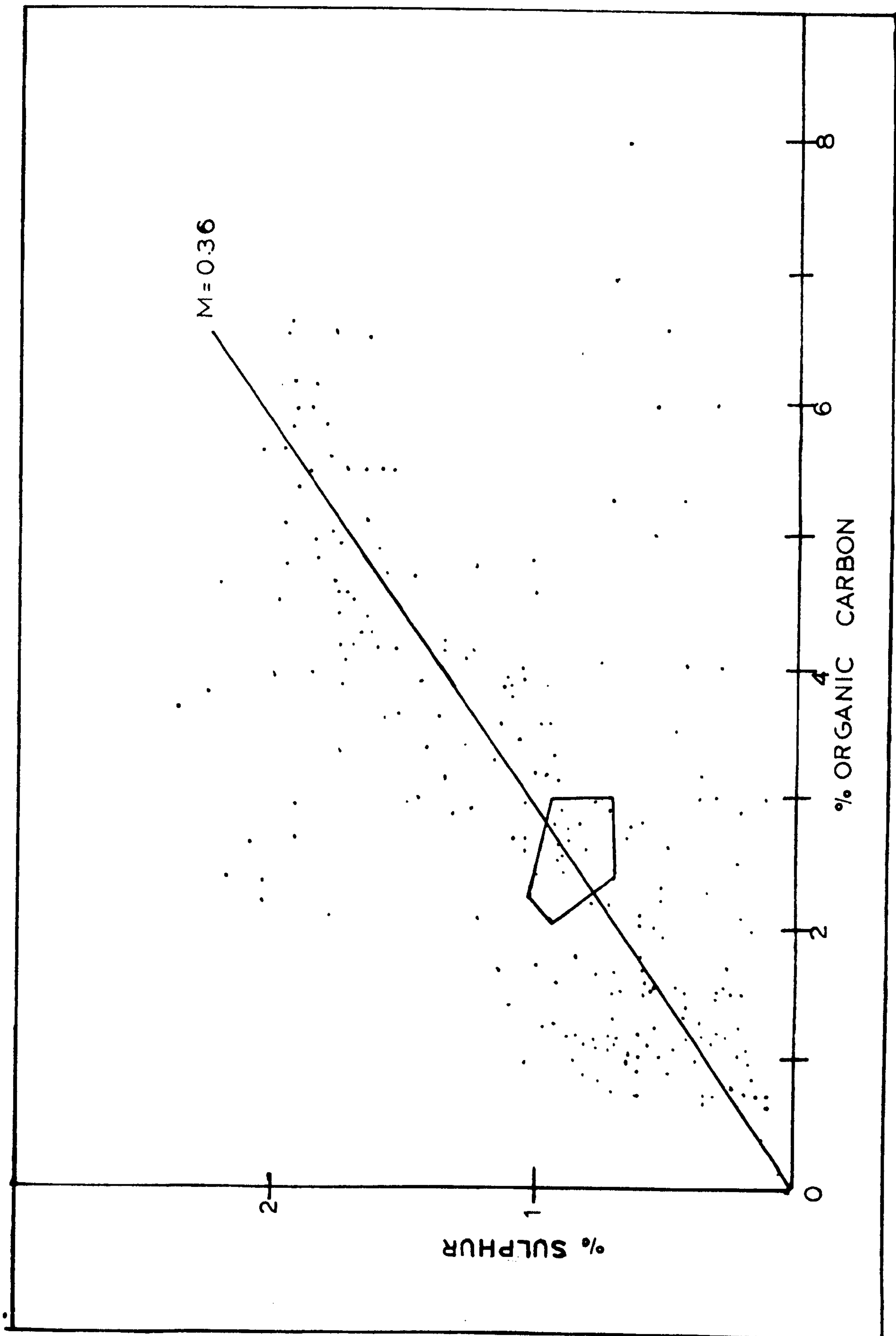
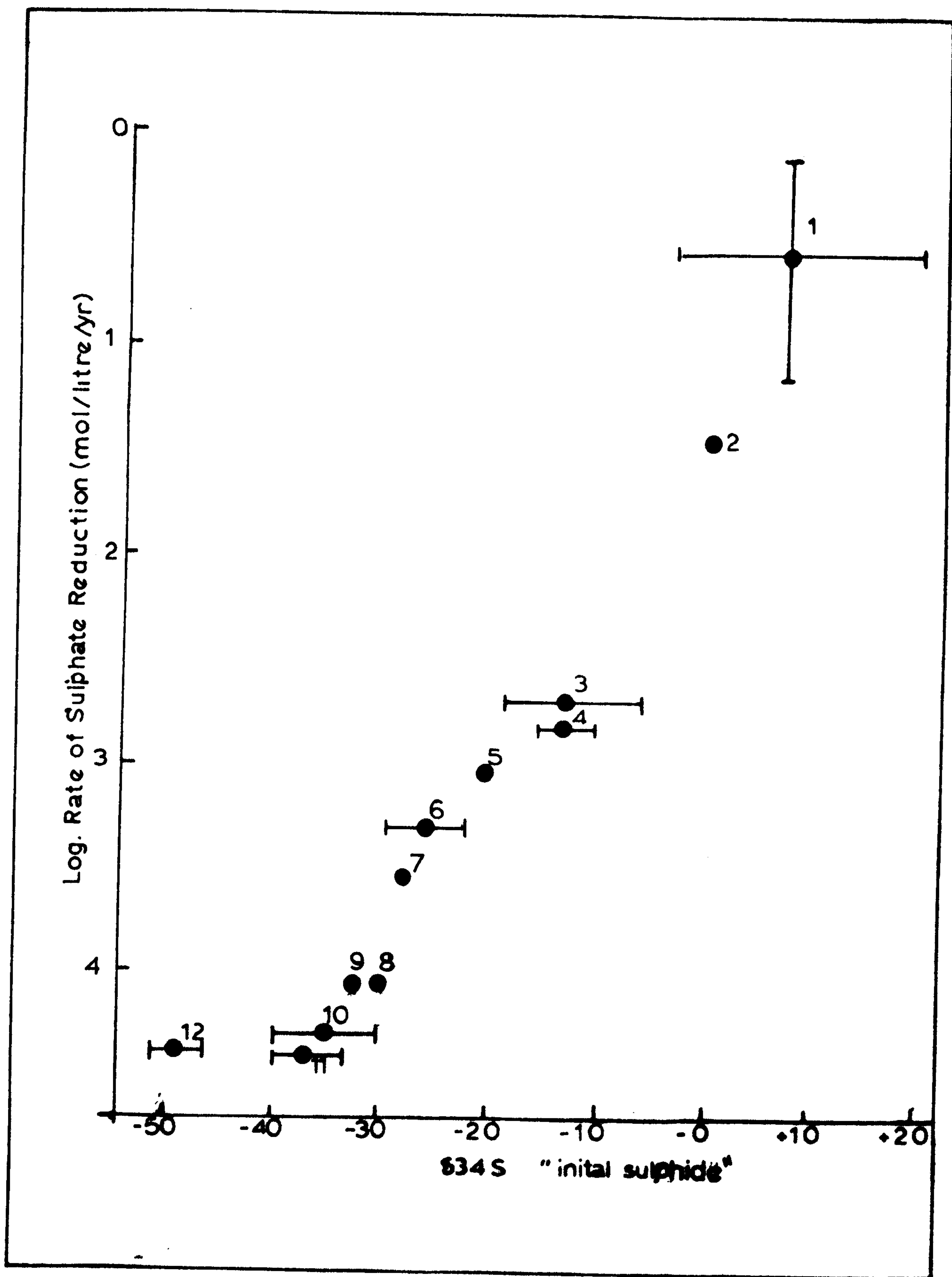
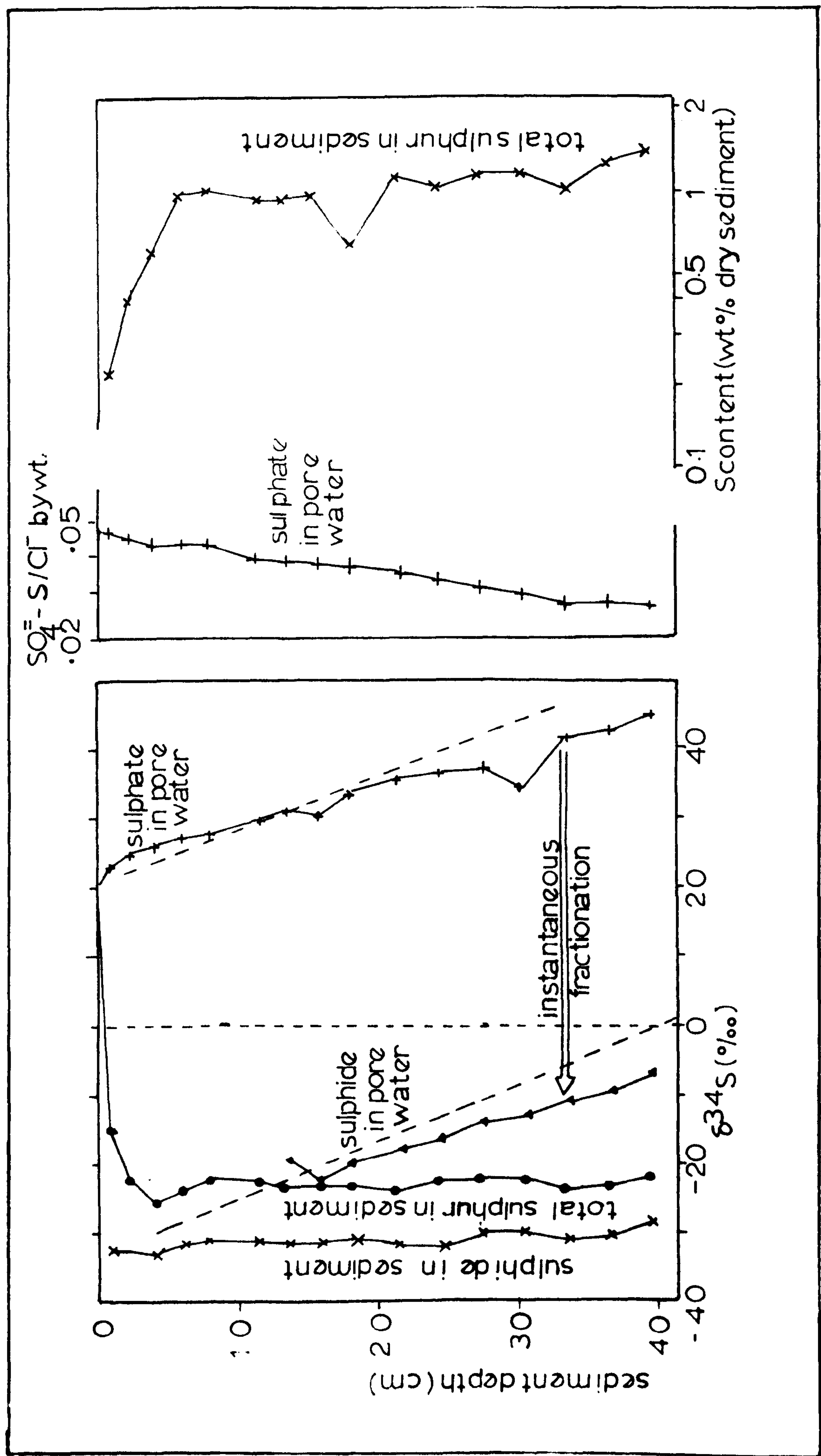


Fig.11 Log. rate of sulphate reduction against  $\delta^{34}\text{S}$  initial sulphide. 1. Various laboratory experiments using pure cultures. 2. Nakai and Jensen (1964). 3. Naria Del Ray Harbour, isotope data Sweeney (1977) rate Goldhaber and Kaplan (1975). 4. Pettaquamscott River Basin, Rhode Island, Orr and Gaines (1974). 5. Newport marsh South California. Isotope data Kaplan et al (1963) rate calculated from Emery (1960). 6. Santa Barbra Basin . Isotope data Sweeney (1972) ,Rate Berner (1972). 7. Carmen Basin Gulf Of California data Goldhaber (1974). 8&9 Pascadero Basin Gulf of California data as 7. 10. Santa Catalina Basin South California Data as 5. 11. East Cortez Basin South California, isotope data Sweeney (1972) rate calculated from Emery (1960). 12. Long Basin California data as 5.





**Fig 12.  $^{534}\text{S}$  variation (left) and increase of  $^{534}\text{S}$  concentration (right) with depth from modern marine sediment from the Baltic Sea of Kiel (Hartmann and Nielsen 1969)**



### Pyrite Formation in some Bioturbated Clays from the Jurassic of Britain

#### 1. Introduction:

The importance of bioturbating macro-fauna on the early diagenesis of marine sediments has been demonstrated, during recent years, by the work of various authors on recent sediments (Goldhaber et al 1977, Aller 1977, Goldhaber and Kaplan 1980, Berner 1980). Sulphate reduction and the formation of pyrite is one set of early diagenetic reactions which is so affected. During the study of the formation of pyrite, its sulphur isotopic composition and the factors which affected them, various Jurassic shales were examined for their pyrite content and its sulphur isotopic composition, organic and carbonate carbon and HCl extractable iron. The mud rocks studied were divisible, on a palaeoecological basis into three distinct facies (Morris 1980), "Normal", "Restricted" and "Bituminous". Of these three the Normal facies shows extensive bioturbation, and it is this facies which is discussed in this chapter. The Restricted and Bituminous facies are discussed elsewhere (Chapters 3 and 4).

The two Normal shales examined during this study were the Upper Oxford Clay of the East Midlands and the Dunans Clay from Staffin Bay on the Isle of Skye. Hudson and Palframan (1969) described the pyrite moulds of

molluscs, chiefly ammonites from the Upper Oxford Clay at Woodham brickpit. They demonstrated that the chief source of sulphur, as in recent sediments, was seawater. They found pyritization to have occurred at shallow depths in the sediment column prior to the compaction of the ammonites. Further, Hudson (1982) illustrated several pyrite morphologies in Upper Oxford Clay ammonites together with specimens from the Lias of Germany, another Normal clay. Quoted  $\delta^{34}\text{S}$  values from Coleman and Hudson (1980) were, bar one ammonite from the Lias, negative and considered to be in agreement with near surface formation.

For this study samples were collected not from Woodham brickpit, which is no longer accessible, but from the London Brick company pit at Warboys in Cambridgeshire (TL308 817). Samples were also collected from the Dunans Clay member of the Staffin Shale formation of Skye (NG473 078) (Sykes 1975).

### 2. Lithologies, Stratigraphy, and Faunas:

2.1 Warboys: 23m of Upper Oxford Clay is seen at Warboys (Horton and Horrell 1971) ranging from the Cardioceras scarburgense subzone to the Cardioceras bukowskii subzone where it is overlain unconformably by Ampthill Clay (Callomon 1968). The upper part of the section from the praecordatum subzone is quite highly weathered. The



rest of the clay is homogeneous, plastic when wet, hard when dry, and ranges in colour from light grey N7 to light olive grey 5Y6/1 (American Geological Institute Rock colour chart) and is devoid of lamination and fissility. The sequence is broken at several horizons by carbonate-rich bands of shale; cementstones. Pyrite-filled burrows are common throughout the section and range in size from 1 to 10mm diameter.

The clay contains an abundant ammonite fauna often as pyritized nuclei. Gryphea is found throughout the sequence, often encrusted with foraminifera (Horton and Horrell 1971). Pyritized Nuculacean bivalves and Dicroloma (a gastropod) are common. Pinna is commonly found in the basal parts of the scarburgense subzone and within the top of the praecordatum subzone: Hudson & Palframan record them as being found in growth position at Woodham. Part of the limitation of the fauna may be preservational; as found by Hudson & Palframan at Woodham, a large number of originally aragonitic fossils, which were not infilled with pyrite, were preserved as clay moulds, which were destroyed in weathering.

2.2 Dunans Clay: The Dunans Clay member (Sykes 1975) is one of the five members of the Staffin Shale formation (Turner 1966). It corresponds in age to the Middle and Upper Oxford Clay of England, ranging from the athleta



zone (phaenium subzone to the cordatum zone (cordatum subzone) (Sykes and Callomon 1979). It consists of 37m of bluish grey silty mudstones 5B4/0.5 to 5B6/0.5 and is marked 2m above the base by two cement-stone concretion horizons. The remaining section is divided into a series of rhythms by the occurrence of dark silty beds which contain an abundance of plant material. At their bases Chondrites mottling is extremely noticeable; it is present throughout the section but the colour difference at these horizons serves to enhance its appearance. Sykes reported that the thicker of these horizons (>2cm) have plain unburrowed bases, although all such horizons looked at in this study appeared to show burrowing at the base. Sykes also reported the tops of these rhythms as often marked by sideritic cement-stones, six of which are reported by Turner (1966), Sykes & Callomon (1979). At point 5 as defined in the Skye memoir (Anderson and Dunham 1964), where the present section was studied only the basal two were present. It is noticeable though that when analysed, the beds directly beneath the dark silty horizons had higher carbonate contents. Bands of small 2 to 3cm phosphate nodules are common throughout the sequence. Phosphate is often associated with ammonites.

Ammonites are highly abundant throughout the section and have a characteristic preservation of the aragonitic shell, with three dimensional body chambers infilled with phosphate, and phosphate concretions often

grow in the umbilicus. Several specimens show three dimensional preservation of the inner whorls with a pyrite internal mould. Some, though, show crushing of the ammonite prior to pyrite formation. The other fauna is somewhat limited. Sykes records a noticeable difference between the dark woody horizons and the other clays: the former containing Oxytoma inequivalvis, which he suggested lived attached to floating wood, the latter contain mainly small Nuculana and Dentalium. Near the top of the section he also records Thracia and Camptonectes. It is worth noting that in hand specimen under the hand lens the clay can be seen to contain many fragments of aragonitic shell, which appear to have been broken and dispersed by bioturbation, although they are not specifically identifiable some show ribbing and ornament not normally associated with nuculaceans. At several horizons particularly within the costicardia subzone foraminifera are seen to be present; these have been studied by Cordey (1962). As mentioned above Chondrites is found throughout the sequence, also horizontal pyrite filled burrows ranging in size from 1 to 5mm, which in appearance are very similar to those found in the Upper Oxford Clay (see above).

### 3. Biofacies and Palaeoecology:

As mentioned in the introduction the Upper Oxford

Clay and the Dunans Clay are both thought to be Normal clays under the Morris (1980) classification. This classification relies on a statistical count of bivalves, and their separation into three groups by mode of life, epifaunal suspension feeders, infaunal suspension feeders, and infaunal deposit feeders. The Normal facies is characterized by a diverse benthic macrofauna of infaunal and epifauna type but deposit feeders constituting less than 20% of the fauna; fig 1 shows the field of Normal clays on a triangular bivalve feeding plot. Statistical counts of the Upper Oxford Clay and Dunans Clay faunas has not been undertaken, and it is possible even if this was done they would show biased counts due to preservational considerations. Both units show a mix of feeding types and are characteristically bioturbated, which is usual in Normal clays. The environment of deposition is thought to be oxidising in the water column and the first 0.5m or so of the sediment and thus to correspond to Morris' Normal facies.

#### 4. Collection, Sample Preparation and Experimental Techniques

Collections were made at intervals throughout both sections and fig 2 shows the localities and sample numbers. Samples for organic and carbonate carbon, fine grained pyrite sulphur isotopes and HCl extractable iron



analyses were prepared as powders. In most cases this was done by drilling the shale from the the hand specimens using a jeweller's drill; in this way inhomogeneities, such as pyrite burrows could be avoided and, where present, light and dark clay could be sampled separately. Some samples for organic and carbonate carbon analyses and acid soluble iron were prepared by grinding in a terna mill, but only when the sample was, apart from small pyrite burrows, homogeneous.

Organic and carbonate carbon analyses were performed using a two stage wet chemical technique, a modification of Bush(1970) (Appendix 1). First carbonate carbon is liberated as  $\text{CO}_2$  by analar phosphoric acid and trapped in standard  $\text{Ba}(\text{OH})_2$  solution; the  $\text{Ba}(\text{OH})_2$  is then back titrated against standard  $\text{HCl}$  solution. The organic carbon is then liberated by the addition of saturated chromic acid to the mixture, the  $\text{CO}_2$  produced is again trapped in  $\text{Ba}(\text{OH})_2$ .

Sulphur for isotopic analysis was quantitatively extracted as  $\text{SO}_2$  at high temperature using cuprous oxide (Robinson & Kusakabe 1975) using an extraction line set up as described by Coleman and Moore(1978). It was found necessary to pre-treat samples with 10% acetic acid to remove carbonate and also to react the sample for 12hrs in an oxygen plasma using a Nanotech Plasmaprep, which serves to oxidize at low temperature ( $150^\circ\text{C}$ ) any organic matter present. Both the carbonate and organic material

would, during the extraction, form  $\text{CO}_2$ , which would interfere with the extraction. The treatment of the sample in the oxygen plasma should serve to remove any organic bound sulphur present. Both the acid and plasma treatments were undertaken quantitatively so that the  $\text{SO}_2$  yield could be used as a measure of the pyrite sulphur content. The  $\text{SO}_2$  was analysed on a V.G micromass 602C mass-spectrometer with heated inlet. Raw data was corrected for instrumental and isobaric effects (Coleman 1980).

HCl extractable iron was determined using a method similar to that of Berner (1970). 0.2g of the powdered sample was boiled for 2min with 3ml of concentrated HCl in a hot block. The liquid was then diluted to 10ml and analysed on a Perkin Elmer Atomic Absorption Spectrometer.

Results are presented in tables 1 and 2, analytical precision was as follows; pyrite sulphur content, although variable, depending on the sample size and the volume of  $\text{SO}_2$  produced, was generally better than 0.1%.

$\delta^{34}\text{S}$ ; the analytical uncertainty in any sulphur isotopic determination is 0.1‰; the reproducibility between two standards extracted and analysed was normally better than 0.2‰. In the case of shale samples the reproducibility was somewhat worse but no more than 0.7‰. Organic and carbonate carbon reproducibilities were better than 0.1%. HCl extractable iron is probably



better than 0.1%.

### 5. Results Results are presented in tables 1&2 and Fig3

5.1 Pyrite sulphur and  $\delta^{34}\text{S}$  Variations: The fine-grained pyrite sulphur content of both the Upper Oxford Clay and the Dunans Clay is small: The values lie between 0.2 and 1.3% S averaging 0.63%. The Dunans Clay has on average a slightly higher S content (0.72%) compared to the Upper Oxford Clay (0.51%). The  $\delta^{34}\text{S}$  values for the fine-grained pyrite in both cases are light (means -36‰, Dunans Clay and -36.9‰, Upper Oxford Clay), and not significantly different. The values range between -42‰ and -19‰, which, with Jurassic seawater at +16‰, represent maximum fractionations of at least -58‰. In the Dunans Clay one pyrite-filled burrow was analysed and yielded a  $\delta^{34}\text{S}$  value of -49.3‰ suggesting an even greater fractionation of -66‰. The spread of the isotope values in the Dunans Clay is noticeably greater than that of the Upper Oxford Clay ( $\sigma=7.20$  compared with 3.44). As can be seen in the histogram it is two Dunans clay samples which have the most positive values of -19.0 and -19.2‰, which are separated by some 10‰ from the next highest values.

5.2. Organic Carbon: Both the Dunans Clay and the Upper Oxford Clay show low organic carbon concentrations generally less than 2% C. The Upper Oxford Clay has a significantly lower %C organic than the Dunans Clay (mean of 0.70% compared with 1.35%). The dark, wood-rich horizons of the Dunans Clay show noticable higher %Cs and the most extreme value of 7.69% (this value has been ignored in the calculation of the mean due to the excessive bias it places on it). The cement-stone horizons from Warboys show lower %C, 0.46 and 0.17%, indicating some dilution by later diagenetic carbonate.

5.3. Carbonate Carbon: The carbonate carbon values are generally high with no significant difference between the two clays (means 2.34 and 3.65% equivalent to 22 and 30% calcium carbonate). The mean for the Upper Oxford Clay excludes the cement stones which have far higher %C carbonate between 7.7 and 8.1% (64 and 67%  $\text{CaCO}_3$ ). It is apparent that the samples from just beneath the wood-rich horizons in the Dunans Clay have higher carbonate carbon values eg. sample SDC81/26A with 4.36% and SDC81/9A with 3.06%.

5.4. Acid Extractable Iron (%FeHCl) and Degree of Pyritization (D.O.P.): %FeHCl values represent the amount of iron, which is present in the sediment, and would have been reactive to  $\text{H}_2\text{S}$ . Berner states that the

method completely dissolves fine-grained hematite, limonite, goethite, and chlorite, and small amounts of silt sized magnetite, goethite, hornblende, augite, biotite and epidote and that the solubility of these minerals in hot HCl is similar to their reactivity with H<sub>2</sub>S. The high concentrations of HCl used in the preparation probably lead to the solubilization of larger quantities of iron than would have reacted with the relatively low concentrations of hydrogen sulphide present in sediments. The values of %FeHCl therefore represent the maximum amount of iron still remaining that could have formed pyrite, if sufficient H S had been present. As well as the values for %FeHCl the degree of pyritization (D.O.P.) has been calculated,

$$D.O.P. = \frac{\%Fe \text{ AS PYRITE}}{\%Fe \text{ AS PYRITE} + \%FeHCl}$$

D.O.P. is a measure of the amount of originally available iron which has formed pyrite. Its value lies between 0 and 1. If no pyrite forms then its value will be 0. If iron is limited then as pyrite forms its value will approach 1.

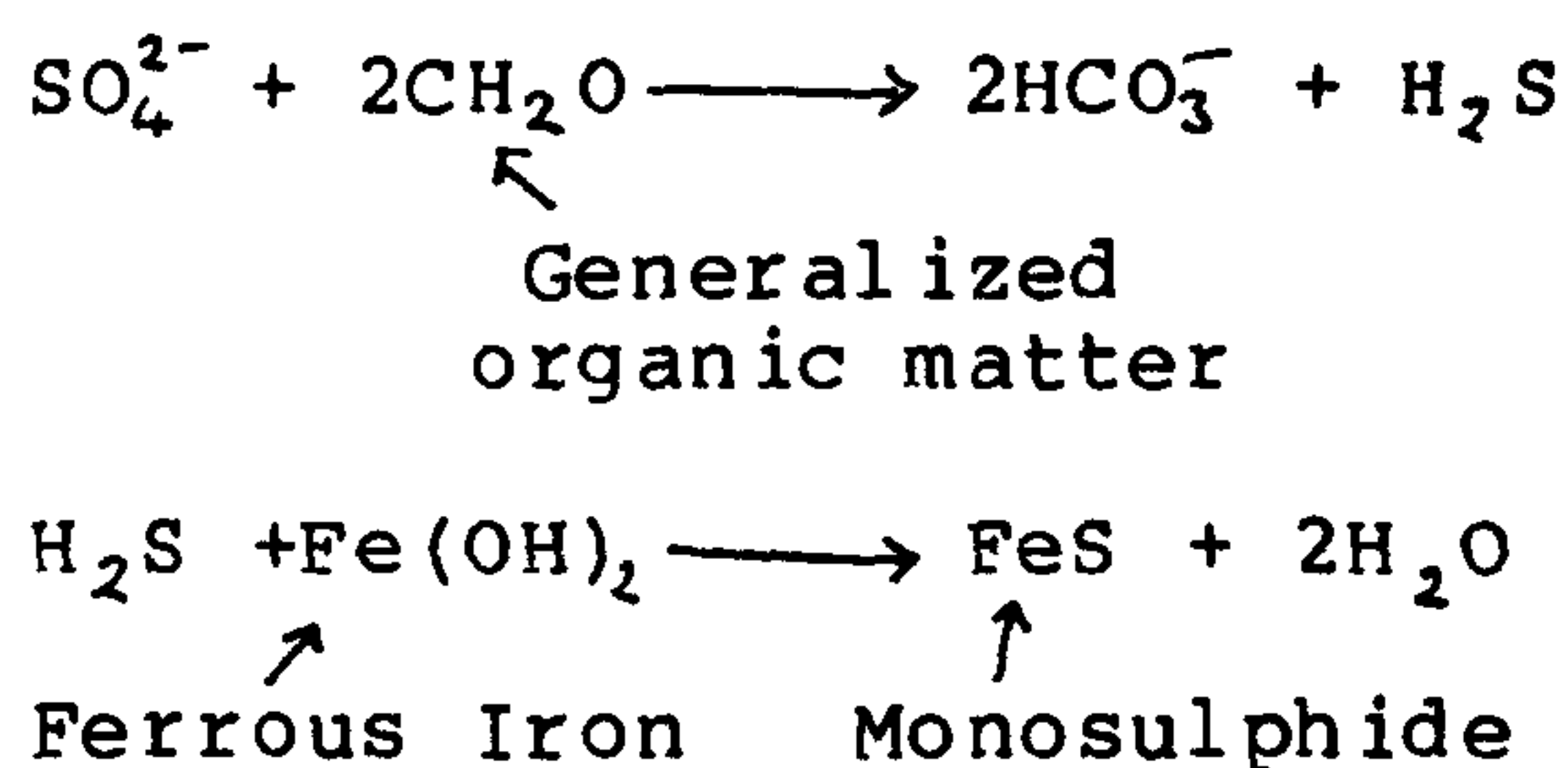
The %FeHCl, for the two clays, lie between 0.5 and 2.5% Fe. The Dunans Clay has significantly higher %FeHCl (mean 1.59) compared to the Upper Oxford Clay (mean 1.08). The D.O.P. are low less than 0.45 and in both clays the mean and standard deviation are the same



( $X=0.29$   $\sigma=0.08$ ). This therefore suggests that more acid extractable iron was present in the Dunans Clay, but as the Dunans Clay has formed on average more pyrite its D.O.P. is similar to that of the Upper Oxford Clay.

#### 6. Controls Of Pyrite Sulphur Content:

The formation of pyrite in marine sediments is due to the action of sulphate reducing bacteria on seawater sulphate to form sulphide, which then reacts with iron to form pyrite, either directly or via a monosulphide phase (Goldhaber & Kaplan 1974). The reactions may be summarized as follows:



The iron monosulphide (mackinawite) may proceed to pyrite by the addition of elemental sulphur (Goldhaber & Kaplan 1974). It has been demonstrated that if the reaction proceeds via a greigite phase the characteristic framboidal texture results (Sweeney & Kaplan 1973), a common form of pyrite in the Upper Oxford Clay (Hudson 1982).

The formation of pyrite involves four prerequisites

1. Anoxic conditions in which the bacteria can function;

sulphate-reducing bacteria are obligate anaerobes. This does not mean, as was commonly suggested in the 1950s, that the clay must be deposited in stagnant euxinic conditions. In the case of the Upper Oxford Clay and the Dunans Clay, with the presence of benthic organisms and abundant trace fossils, this is demonstrably not the case. Within the sediment dissolved oxygen in the pore water will be exhausted by the action of aerobic bacteria producing anaerobic conditions within the sediment. The action of burrowing organisms may serve to alter the chemistry of the surface layers in which they live. They irrigate the sediment with overlying oxic water, which may then diffuse outwards from the burrows to be exhausted in the interburrow sediment (Goldhaber & Kaplan 1980, Aller 1977). Within the upper bioturbated parts of the sediment oxic conditions can be maintained in an otherwise anoxic sediment. Similarly within generally oxic sediments organic-rich microenvironments, i.e. disused burrows or faecal pellets, or enclosed voids, such as ammonite chambers, may form localised anoxic conditions in which sulphate reduction can occur in an otherwise non reducing sediment (Kaplan Emary & Rittenberg 1963, Hudson 1982).

2. Sulphate. Seawater sulphate is the chief source of sulphate used by bacteria in the formation of pyrite. In the surface bioturbated horizons the sulphate is added

to the sediment by mixing and irrigation, which serves to keep the concentration of sulphate close to that of seawater. Beneath the zone of bioturbation sulphate is added by diffusion, the diffusion gradient being controlled by the rates of bacterial reduction (Berner 1980).

3. Organic matter is necessary as the material on which the bacteria feed. Various laboratory experiments indicate that the rate of sulphate reduction is dependent on both the quantity and quality of organic matter. Harrison & Thode (1958) found that high rates of reduction were associated with high concentrations of organic matter. A general covariance between pyrite sulphur content and organic matter concentration has been noted by several authors (Berner 1970, Sweeney 1972, Goldhaber and Kaplan 1974). This general covariance has been attributed to higher initial concentrations of organic matter giving rise to larger quantities of pyrite sulphur, and if the amount of organic matter utilized in sulphate reduction is a constant proportion of the total initial organic matter entering the sulphate reduction zone then a linear correlation between organic carbon and pyrite sulphur will result. Sweeney (1972) produced a compilation of data from recent sediments and found an C/S ratio of about 3. For the proportion of organic matter utilized



in sulphate reduction to be constant the composition of organic matter entering the sediment must be similar from one area of deposition to another. Postgate (1965,1979) suggested that sulphate reducing bacteria in laboratory cultures utilize only a limited range of organic compounds, mainly short chain carboxylic and amino acids. It may well be that in natural sediments they can and do utilize a wider range of compounds either directly or via the action of other bacteria. The relationship between organic carbon and pyrite sulphur should reflect therefore the proportion of organic matter which is utilizable by the sulphate-reducing bacteria.

The composition of organic matter entering the sulphate reduction zone will depend highly on the environment through which it has passed. It will have been acted on by aerobic bacteria, which will serve not only to reduce the total organic matter, but also, as aerobic bacteria also prefer the short chain carboxylic acids, will reduce the the proportion of organic matter utilizable by the sulphate-reducing bacteria (Zolnay 1971).

4. Iron is necessary for the conversion of  $H_2S$  into iron sulphide. Iron is supplied to the sediment in detrital minerals and as iron oxide coating on grains, and is in the ferric form.  $H_2S$  may react in situ with

ferric iron and simultaneously reduce it and precipitate FeS (Berner 1969, Sweeney 1972). When all the in situ iron is consumed H<sub>2</sub>S will be free to diffuse away from the site of reduction, iron is only soluble when in the ferrous form. If the sediment is generally oxic and the site of reduction is a microenvironment iron will not diffuse inwards and the H<sub>2</sub>S produced will be free to diffuse away into the surrounding oxic sediment, where it will be reoxidized. Therefore even if the sediment as a whole is iron-rich the pattern of oxic and anoxic environments may not allow the trapping of all H<sub>2</sub>S produced. If the sediment becomes anoxic then the total amount of iron present will become important. If sufficient organic matter and sulphate are present to maintain a high concentration of H<sub>2</sub>S the total amount of pyrite formed will be limited by the iron and the D.O.P. will approach 1 (Berner 1970). The availability of iron may control the amount of pyrite precipitated and the stage at which it is precipitated in the sediment column.

### 7. Controls Of $\delta^{34}\text{S}$ Variation

Three main factors may affect the  $\delta^{34}\text{S}$  value of fine-grained pyrite formed in clays and shales:

1. Instantaneous fractionation factors between the sulphate and sulphide.
2. The  $\delta^{34}\text{S}$  value of sulphate. The chief source of

sulphate is sea water which in the Jurassic had a  $\delta^{34}\text{S}$  of about +16‰ (Claypool et al 1980). If though sulphate reduction occurs in a closed or partially closed system the sulphate sulphur will become enriched in  $^{34}\text{S}$  due to the formation of isotopically light sulphide. The  $\delta^{34}\text{S}$  value of sulphate may change if significant amounts of sulphate are added from a source which is isotopically different to that of seawater e.g. light sulphate from the reoxidation of sulphide in zone of bioturbation and mixing.

3. The proportion of sulphide formed at each stage of burial, either within an open system or a closed system.

Fractionation factors for the bacterial reduction of sulphate have been experimentally studied by several authors (a good review is given by Chambers & Trudinger 1979). Experiments have shown a wide range of isotopic effects between +3 and -46‰ (sulphide-sulphate) and indicate that the greatest fractionations are obtained at the lowest specific rates of reduction. The smallest fractionations (+3‰) were obtained at low concentrations of sulphate (0.01 millimolar) (Harrison and Thode 1958). It has been suggested that at extremely low rates of reduction of reduction fractionation may approach equilibrium values of -74‰ at 25°C (Tudge & Thode 1950, Trudinger & Chambers 1973). Although at such slow rates of reduction the quantity of sulphide formed



should be small. A compilation of apparent fractionation factors given by Chambers and Trudinger (1979) indicate that fractionations in recent sediments range between -34 and -59‰ with a mean of about -50‰. These values are generally more negative than those found in laboratory experiment. This might suggest that specific rates of reduction in natural sediments are much slower than those found in laboratory cultures. Alternatively these apparently large fractionation factors may be the result of the addition of isotopically light sulphate from the reoxidation of sulphide.

The chief source of sulphate is seawater which in Jurassic times had a  $\delta^{34}\text{S}$  value of +16‰. If sulphate reduction is taking place in a totally open system, with respect to sulphate, then the sulphate reservoir can be considered to be more or less infinite and the removal of isotopically light sulphide will not noticeably affect the  $\delta^{34}\text{S}$  value of the sulphate. A totally open system may result from reduction occurring in the water column, or within the sediment when bioturbation and mixing act to move large quantities of water through the sediment. On further burial the sediment becomes closed to the access of seawater and the addition of sulphate is limited to diffusion, in this case the preferential removal of  $^{32}\text{S}$  by the bacteria serves to enrich the sulphate in  $^{34}\text{S}$ . If reduction goes to completion the resulting sulphide

would be expected to have the isotopic composition of the initial sulphate. It has been demonstrated that the preferential removal of  $^{32}\text{S}$  enhances the diffusion gradient for  $^{32}\text{S}$  and so the resulting sulphide is significantly lighter than the supposed seawater value (Goldhaber & Kaplan 1980). The resultant value is somewhere in the region of Seawater-25‰, assuming a fractionation factor of -45‰.

In the surface layers of the sediment where bioturbation and mixing juxtapose oxic and anoxic environments, reoxidation of reduced sulphur compounds, mainly iron monosulphides, may occur. Aller (1977) found that on average about 60% of the total reduced sulphide is reoxidized. As the sulphides are isotopically lighter than the seawater sulphate and sulphide oxidation occurs without a significant fractionation (Nakai & Jansen 1964), the refluxed sulphide may act as a source of isotopically light sulphate for further reduction. Goldhaber and Kaplan (1980) found in one core from the Gulf Of California that sulphate in the top 40cm was increased by some 5mM and depleted by 3‰ indicating the reoxidation of sulphide; Goldhaber and Kaplan suggested that this might be a handling phenomenon. Benmore et al (1983) looking at the structural sulphate in francolite found  $\delta^{34}\text{S}$  values depleted by some 10‰ relative to sea water sulphate which suggested the assimilation of reoxidized light sulphide.



There are therefore within the sediment two zones in which sulphate reduction may occur:

1. An upper zone of bioturbation and mixing
  2. A lower zone where sulphate is supplied by diffusion.
- The former is essentially an open system where sulphide forms at seawater-50‰ (The Chambers and Trudingers mean value). The latter is partially closed and so sulphide becomes progressively enriched leading, on total reduction of sulphate, to sulphide at seawater-25‰ (Goldhaber & Kaplan 1980). The final sulphide has therefore the isotopic sum of these two zones together with the small amount of sulphide formed from sulphate trapped in the sediment on burial at seawater‰. Goldhaber and Kaplan were able to model  $\delta^{34}\text{S}$  values for the Gulf of California using this method. The isotopic sum assumes that sulphate reduction goes to completion and that sulphate is exhausted prior to organic-C or Fe if the latter two should prove limiting then the sulphide formed in the zone of diffusion will be significantly lighter than the seawater-25‰ value.

### 8. Controls of Sulphate Reduction and $\delta^{34}\text{S}$ in the Upper Oxford Clay and the Dunans Clay

The light  $\delta^{34}\text{S}$  values suggest that the majority of the sulphide was formed in the open system of the zone of bioturbation and mixing, with normally very little forming in the zone of diffusion. The values suggest

fractionations as large as -58‰. The pyrite sulphur contents of both the Upper Oxford Clay and the Dunans Clay are low and suggest a strict limitation on the formation of pyrite. The three possibilities for limiting the formation of pyrite are lack of either Fe, Organic-C or sulphate. Sulphate does not appear to have been limiting during the formation of pyrite as the isotopes indicate open system conditions. As the D.O.P. in both sediments is less than 0.45 this suggests that iron was not limiting. Also if Fe was limiting then not all the  $H_2S$  produced would be trapped as pyrite, which would result in a C/S ratio greater than the average (3). In fig 4 it can be seen that the C/S ratios for these clays is in fact less than 3. It would seem therefore that iron is not limiting. The limiting factor would appear therefore to be organic-C. Both the clays are relatively poor in organic-C probably due to the effects of supply and the consumption of the carbon by aerobic bacteria prior to entering the sulphate reduction zone.

It is noticeable that although the wood-rich horizons of the Dunans clay have higher %C-organics they do not possess the higher %S-pyrite. This may be accounted for by the nature of the organic matter. Woody land plants contain lower proportions of metabolisable organic matter and so lead to higher C/S ratios. Even the lighter non-woody layers of the Dunans Clay have a

higher average  $\delta C$ -organic, than the Upper Oxford Clay. They also have a correspondingly higher  $\delta S$ -pyrite. Higher  $\delta C$ -organic in the Dunans Clay allowed sulphate reduction to continue for longer and to greater depths in the sediment and, in some cases, into the zone of sulphate diffusion where sulphate was isotopically enriched, this is indicated by the more positive  $-19\text{‰}$  values. Later sulphide formation is supported by the presence of ammonites in the Dunans Clay showing post compactional pyrite formation.

It remains still to explain the large fractionations found within these Normal clays, on average  $-52\text{‰}$  but up to  $-58\text{‰}$  in the fine-grained pyrite and  $66\text{‰}$  in the pyrite-filled burrow. These values are larger than the largest experimental values although they correspond with those recorded by Chambers & Trudinger (1979) for recent sediments. These light values may result from isotopic exchange between sulphate and sulphide. At equilibrium values in excess of  $-70\text{‰}$  are predicted but these rely on extremely slow rates of reduction. To produce a value of  $-58\text{‰}$  by the addition of sulphide at  $-70\text{‰}$  to sulphide at  $-45\text{‰}$  it is necessary to add a greater quantity of  $-70\text{‰}$  than the initial  $-45\text{‰}$ . This is hard to justify, as the  $-70\text{‰}$  sulphide should represent a small, last gasp production. Even if these low  $\delta^{34}S$  values were reached they should not contribute significantly to the overall isotopic sum. A second



method of isotopic exchange is by reoxidation and re-reduction of isotopically light sulphide. Aller (1977) demonstrated that reoxidation did occur and has a significant affect on  $\text{Fe}^{2+}$  concentrations. It is reasonable to suppose that if the reoxidation can affect the  $\text{Fe}^{2+}$  it will also affect the sulphate. Experiments by Aller show that initially constant depth/S-concentration profiles are affected by sulphate reduction lowering the S-concentration at depth. In the same profiles an increase of S-concentration is seen in the surface layers, which must surely be due to the reoxidation of sulphide brought from depth by the burrowing organism. The increase is about  $1/20^{\text{th}}$  of the initial sulphate concentration. If the excess sulphate is made up of light reoxidized sulphide at  $-40\%$  then the effect on the sulphate will be very noticeable:

$$\begin{aligned}\text{sulphate } \delta^{34}\text{S} &= \frac{-1/20 * 40 + 1 * 16}{21 / 20} \\ &= \underline{+13.33\%}\end{aligned}$$

this is insufficient to account for the greater than  $10\%$  reductions in the apparent fractionations. For those it is necessary to increase the sulphate concentration by  $1/4$  from approx  $24 \mu\text{moles/cc}$  to  $30 \mu\text{moles/cc}$ , which is only slightly greater than the increase found by Goldhaber and Kaplan in the Gulf of California core.

## Chapter 2

To model fully this mixing of light and heavy sulphate some idea of the rates of sulphate reduction and sulphide oxidation is necessary, and to compare these to the flows of seawater through the sediment. Aller's work suggests that about 50% of the pyrite is reoxidised per year and that in some cases greater than 60% of the total sulphide is reoxidized. If the system is totally open as has been previously supposed then the residence time of sulphate in the sediment should be negligibly small, so that no matter how fast the reoxidation takes place the light sulphide will not build up in the sediment. From the isotopic data of Benmore et al (1983) it does appear that isotopically light sulphide does build up in the sediment. Therefore the sediment cannot be a totally open system. At the same time that the concentration of isotopically light sulphate is building up in the sediment, the accumulation of isotopically heavy sulphate, produced due to the precipitation of the light sulphide, is not wanted. The key to the apparent paradox, of the ability of the sediment to retain light sulphate but allow the residual heavy sulphate to go may lie in the juxta-positioning of oxidizing and reducing environment together by the action of burrowing organisms. The formation of pyrite at seawater-66‰ in the burrow is probably an effect of the specific environment of burrows, which Aller has likened to a miniature acid



mine drainage system, where relatively large amounts of sulphide are reoxidized and so produce anomalously light sulphate in the burrow.

### 9. Conclusions

The Dunans and Upper Oxford Clay are two characteristic Normal clays; they are distinguished by their low %C-organic and %S-pyrite values and negative  $\delta^{34}\text{S}$  values (generally less than 2‰C, 1.3‰S, and -29‰  $\delta^{34}\text{S}$ ). The light isotopic values result from the majority of sulphide being formed in the surface layers where burrowing organisms mix the sediment and overlying water. The juxtaposing of aerobic and anaerobic in this layer of the sediment allows sulphide to be reoxidised and serve as a source of isotopically light sulphate. The sulphide produced therefore appears anomalously light compared to seawater. The formation of sulphide at greater depth in the sediment is limited by the insufficiency of organic material. The slightly more organic-rich Dunans Clay does show evidence of the continuation of sulphate reduction into the underlying zone, where sulphate supply is controlled by diffusion. The organic-rich horizons in the Dunans Clay do not yield significantly higher pyrite contents due to the majority of the material being derived from land plants and so containing less metabolisable organic carbon. The

cycles seen in the Dunans Clay may be related to the availability of terrestrially-derived sediment.

Normal clays are sediments in which the upper layers are inhabited by burrowing organisms, which in turn help to keep the sediment oxygenated. The oxic nature of the sediment and the action of the infaunal inhabitants serve to limit the formation of pyrite and to produce the large fractionations. The formation of pyrite is limited by the availability of organic matter due to its consumption by aerobic bacteria. The formation of pyrite is further limited by the large amount of sulphide reoxidation which occurs in the bioturbated sediment. It is likely that the values for the Dunans Clay and the Upper Oxford Clay are characteristic for all Normal clays. Comparing the isotopic data with that of Coleman and Hudson (in prep) for the lias  $\delta$  ; light values appear to be characteristic for the fine grained pyrite in Normal clays.

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- Fig 3. Histograms of Data from the Upper Oxford Clay (plain squares) and the Dunans Clay (hatched sq) cementstone horizons in the U.O.C are indicated by Cs. Os and Ds indicate the means for the two clays on each plot. A. Organic Carbon  $O=0.70, \sigma=0.27$ ;  $D=1.35, \sigma=0.55$ . B Carbonate Carbon  $O=3.65, \sigma=0.47$  (Cementstones excluded);  $D=2.34, \sigma=0.92$ . C Pyrite Sulphur  $O=0.51, \sigma=0.17$ ;  $D=0.72, \sigma=0.26$ . D HCl Soluble Iron  $O=1.08, \sigma=0.17$ ;  $D=1.59, \sigma=0.42$ . E  $\delta^{34}S$   $O=-36.9, \sigma=3.44$ ;  $D=-36.0, \sigma=7.20$ . F Degree of

## Chapter 2

Pyritization  $O=D=0.29$ ,  $=0.08$ .

Fig 4. Plot Of %S pyrite vs %C organic carbon.

• Upper Oxford Clay, + Dunans Clay

Table 1

## UPPER OXFORD CLAY DATA

SAMPLE	%S Pyrite	$\delta^{34}\text{S}$	%C Carbonate	%C Organic	%Fe	DOP.
OCW82/1	0.5	-36.0	3.52	0.82	0.98	0.31
OCW82/2	0.2	-36.6	7.82	0.46	0.87	0.17
OCW82/3	0.6	-36.6	3.85	0.52	1.06	0.33
OCW82/4	0.5	-34.1	3.58	0.72	1.17	0.27
OCW82/5	0.8	-41.5	3.46	0.92	0.97	0.42
OCW82/6	0.7	-34.5	3.24	0.90	1.04	0.37
OCW82/7	0.5	-29.3	4.73	0.64	0.84	0.34
OCW82/8	N.D	N.D	2.99	0.67	N.D	N.D
OCW82/9	0.3	-39.2	8.03	0.38	1.01	0.21
OCW82/10	0.6	-34.1	4.11	0.74	1.05	0.33
OCW82/11	0.5	-37.6	3.84	0.86	1.30	0.25
OCW82/12	0.5	-38.8	3.36	1.21	1.29	0.25
OCW82/13	N.D	N.D	8.08	0.17	N.D	N.D
OCW82/14	0.6	-40.3	7.73	0.48	1.09	0.33
OCW82/15	0.3	-41.3	3.48	0.98	1.41	0.16

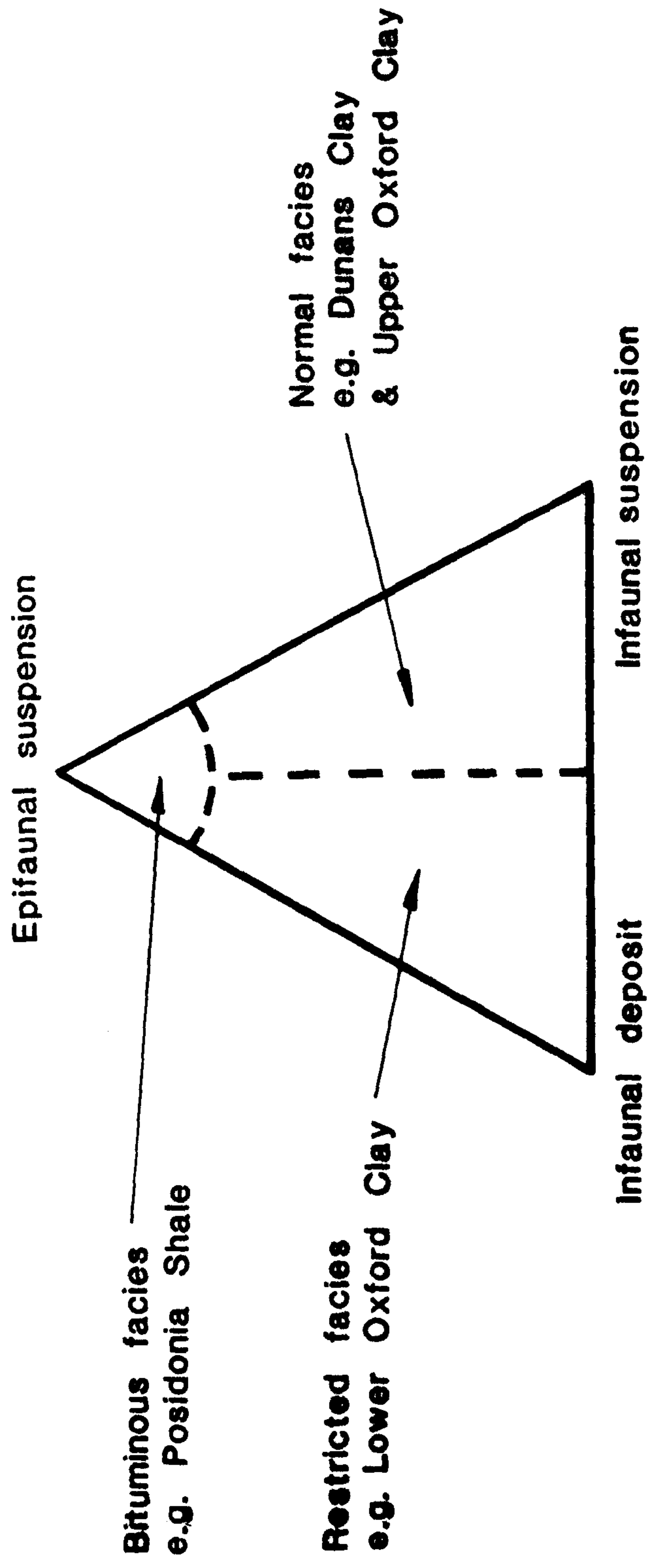


Table 2

## DUNANS CLAY DATA

SAMPLE	%S Pyrite	$\delta^{34}\text{S}$	%C Carb- onate	%C Organic	%Fe	DOP
SDC81/1	0.7	-38.7	2.04	0.60	1.83	0.25
SDC81/3	0.6	-39.3	2.06	0.61	1.96	0.21
SDC81/17	1.1	-33.9	1.46	1.50	1.78	0.35
SDC81/18A	0.9	-35.0	1.48	1.25	N.D	N.D
SDC81/18B	3.7	-49.3	N.D	N.D	N.D	N.D
SDC81/7	0.4	-41.4	1.02	1.55	0.95	0.27
SDC81/9A	0.5	-39.2	3.06	0.82	N.D	N.D
SDC81/9B	0.5	-33.2	2.48	2.59	N.D	N.D
SDC81/19	0.9	-41.0	1.59	1.54	1.42	0.36
SDC81/20	0.7	-34.0	3.20	0.95	N.D	N.D
SDC81/13	1.1	-19.0	1.62	1.47	1.28	0.43
SDC81/21	0.6	-37.5	2.96	1.62	1.47	0.26
SDC81/22A	0.5	-34.6	N.D	N.D	2.23	0.16
SDC81/22B	0.6	-19.2	N.D	N.D	2.30	0.19
SDC81/23	0.9	-34.2	2.01	1.71	N.D	N.D
SDC81/24	0.4	-29.4	1.72	7.69	0.84	0.29
SDC81/25	0.8	-41.5	1.82	1.11	N.D	N.D
SDC81/26A	0.5	-40.8	4.36	1.37	1.66	0.21
SDC81/26B	1.3	-37.1	3.78	2.12	1.64	0.41
SDC81/27	0.7	-41.6	3.04	0.72	1.31	0.32

FIGURE 1



SHALES CLASSIFIED BY BIVALVE ECOLOGY ( After Morris 1980 )

Fig 2. Sections of the Dunans Clay Staffin Bay Isle of Skye and the Upper Oxford Clay Warboys, Cambridgeshire. Numbers indicate sampling site. Dunans clay sample prefixes SDC81/. Upper Oxford Clay prefixes OCW82/. Black lines on the Upper part of the Dunans Clay section indicate wood-rich horizons.

fig 2

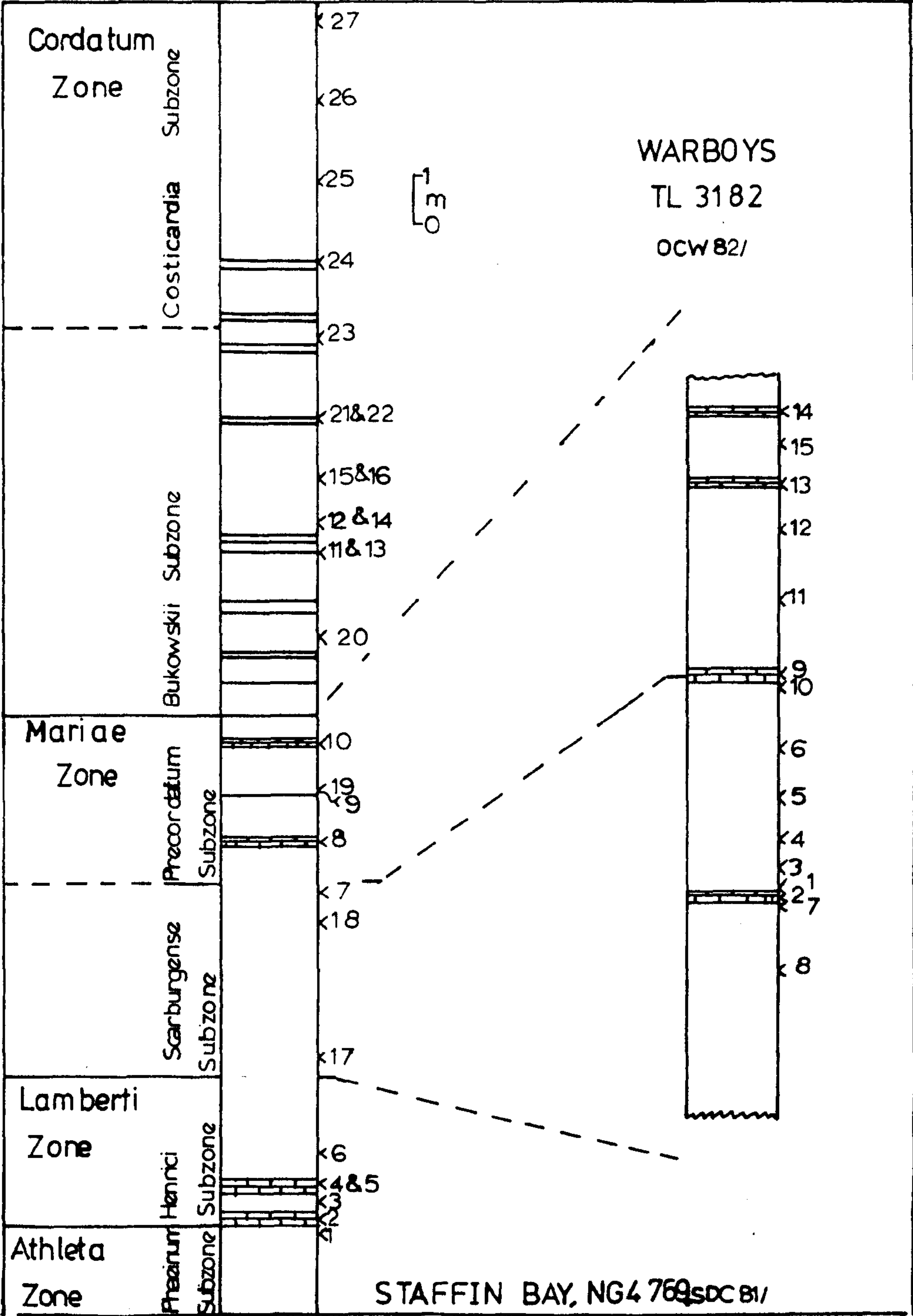
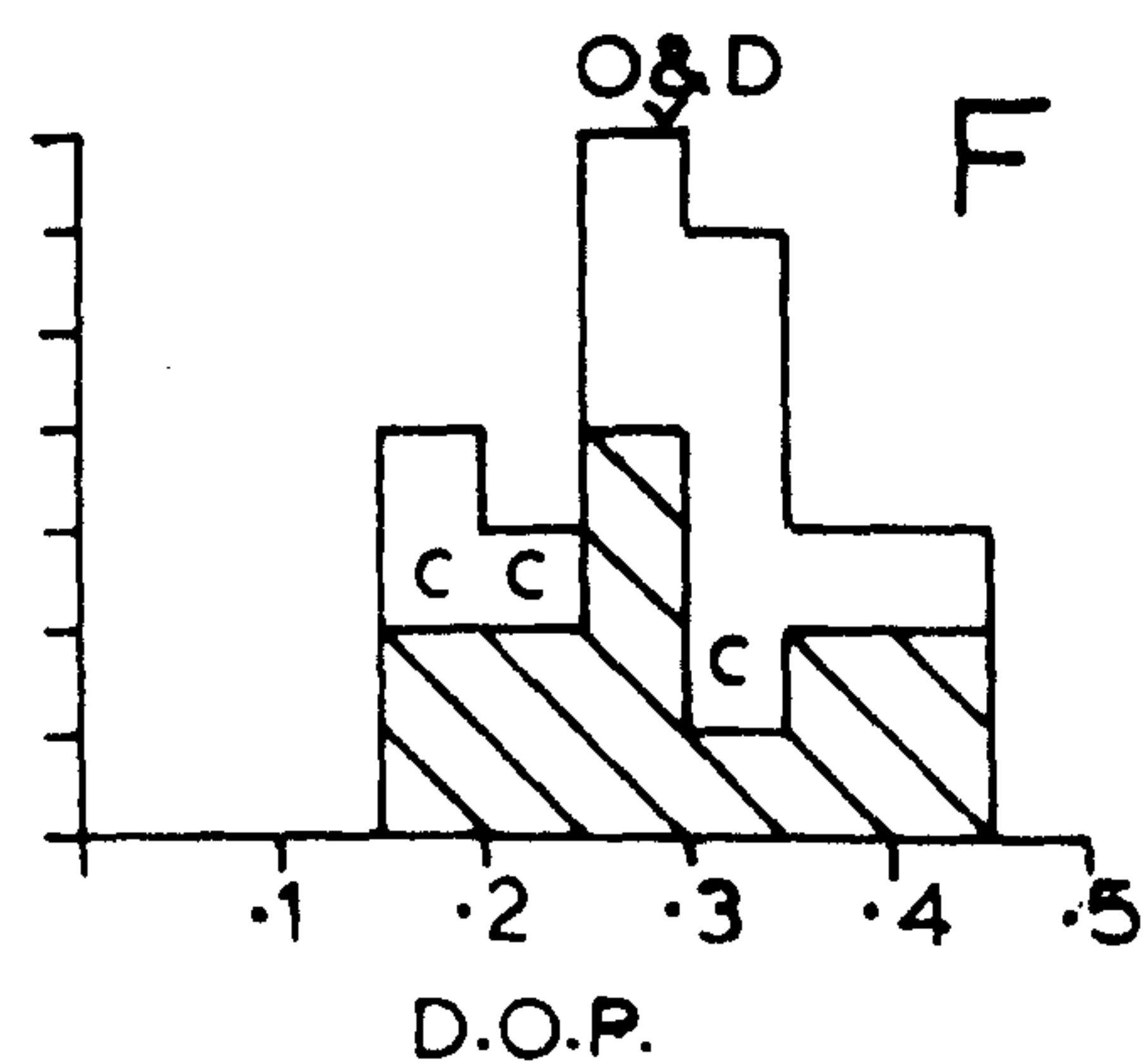
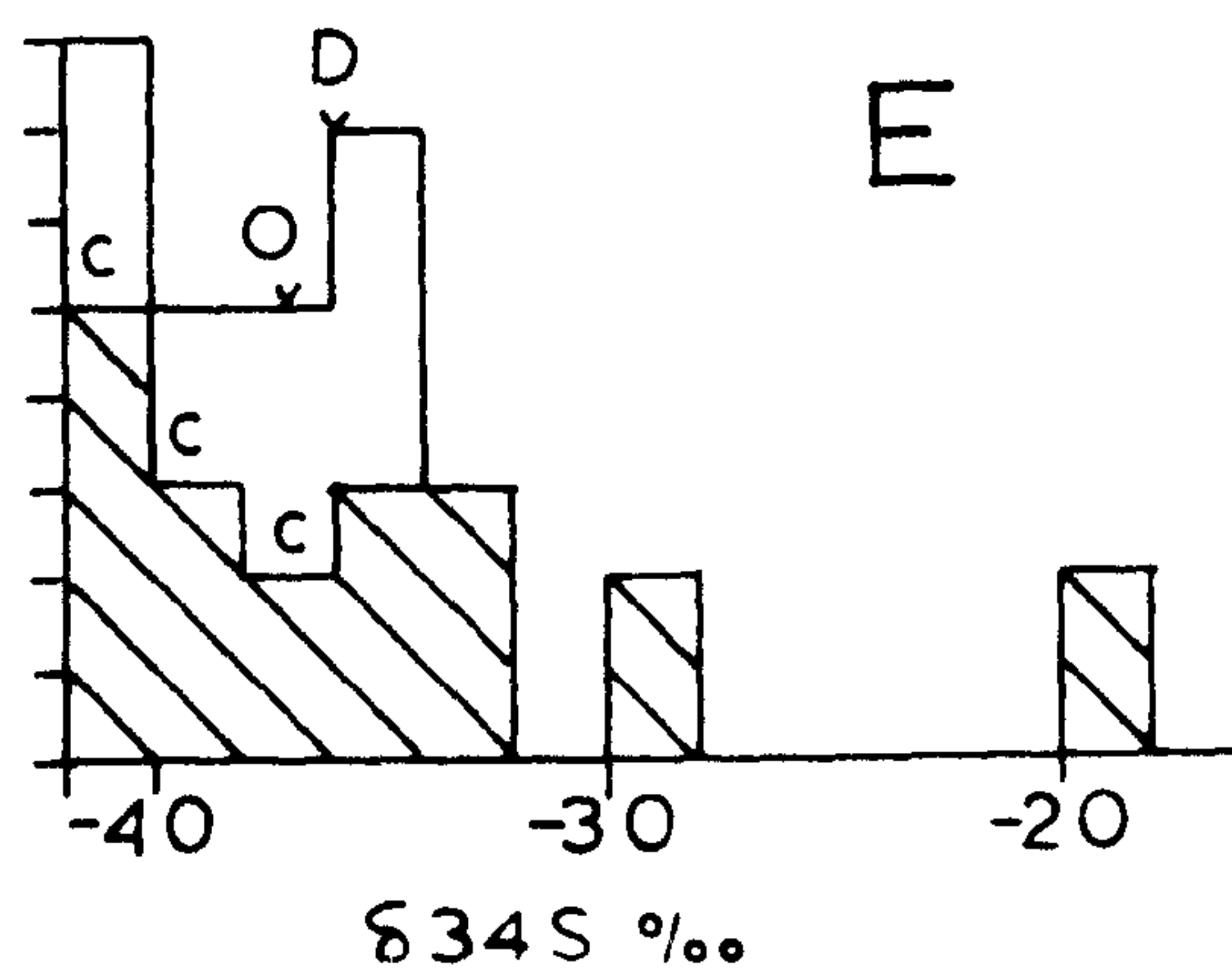
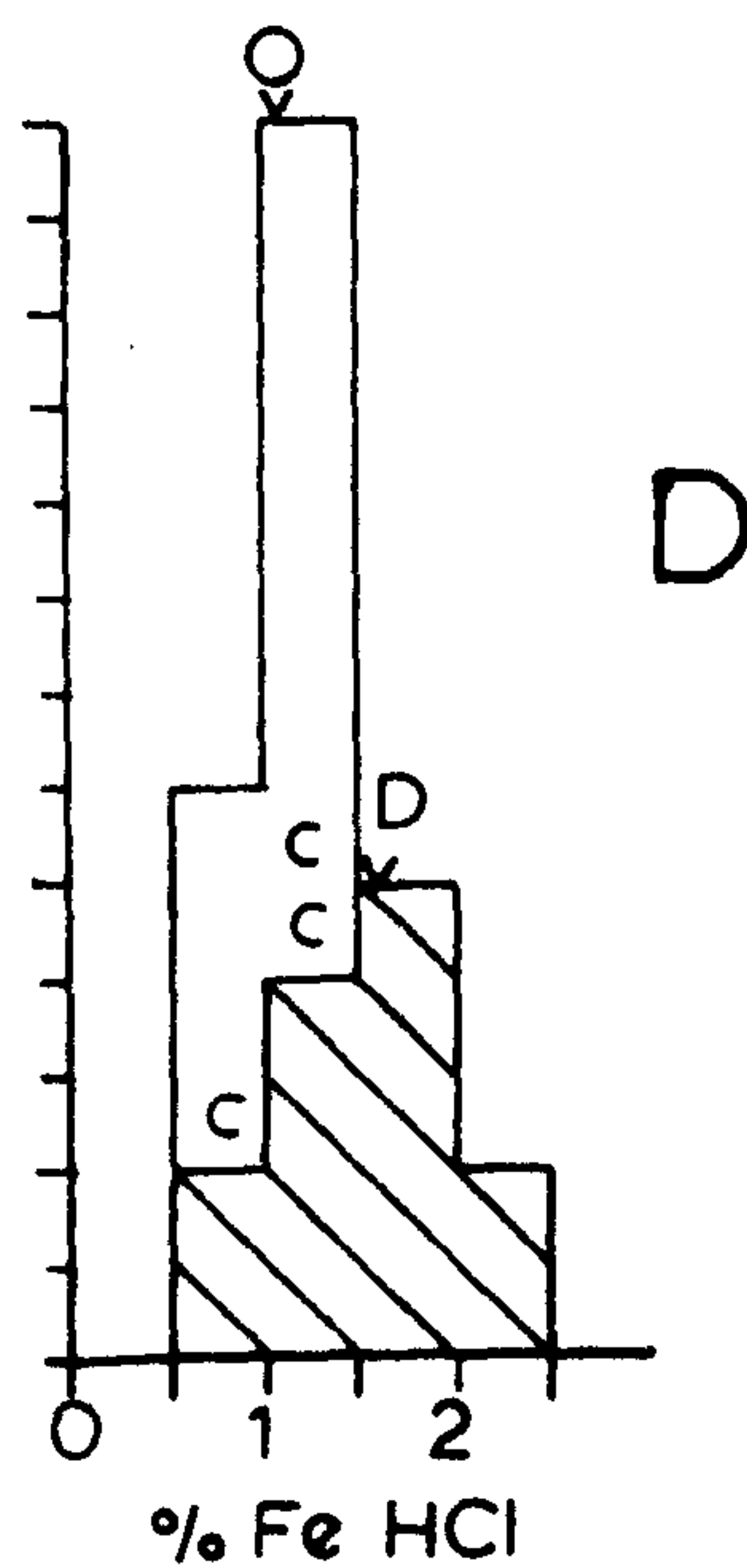
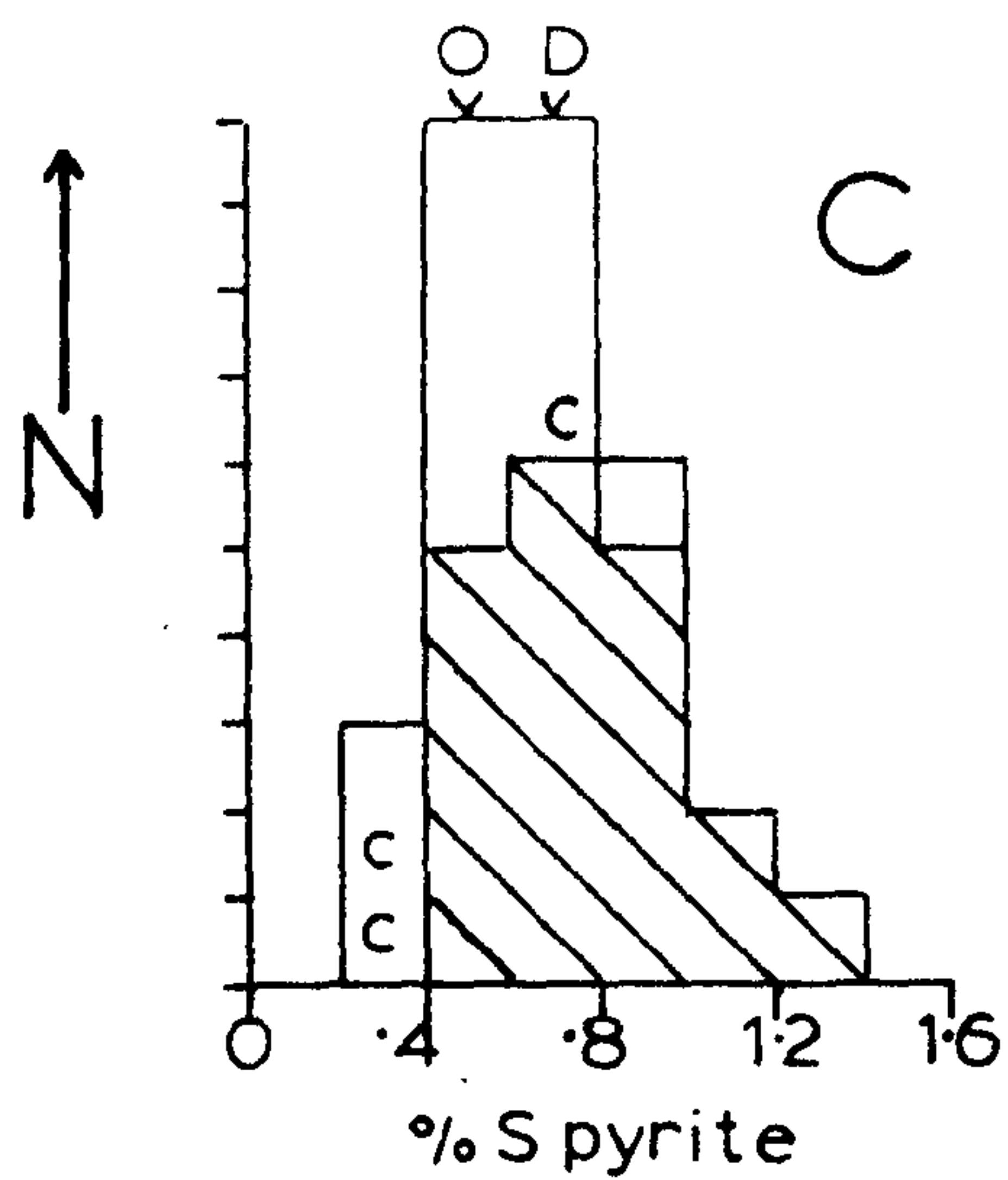
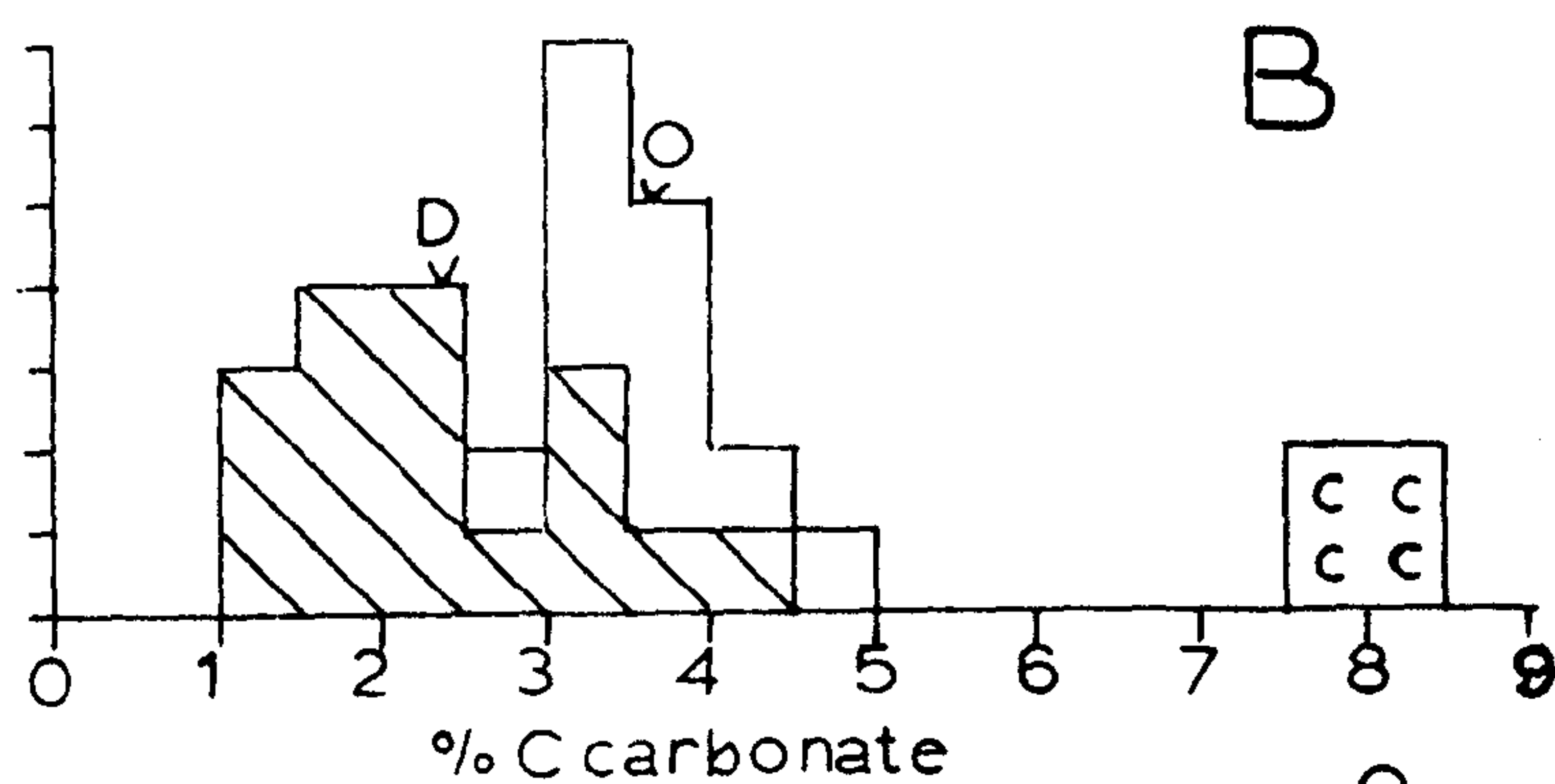
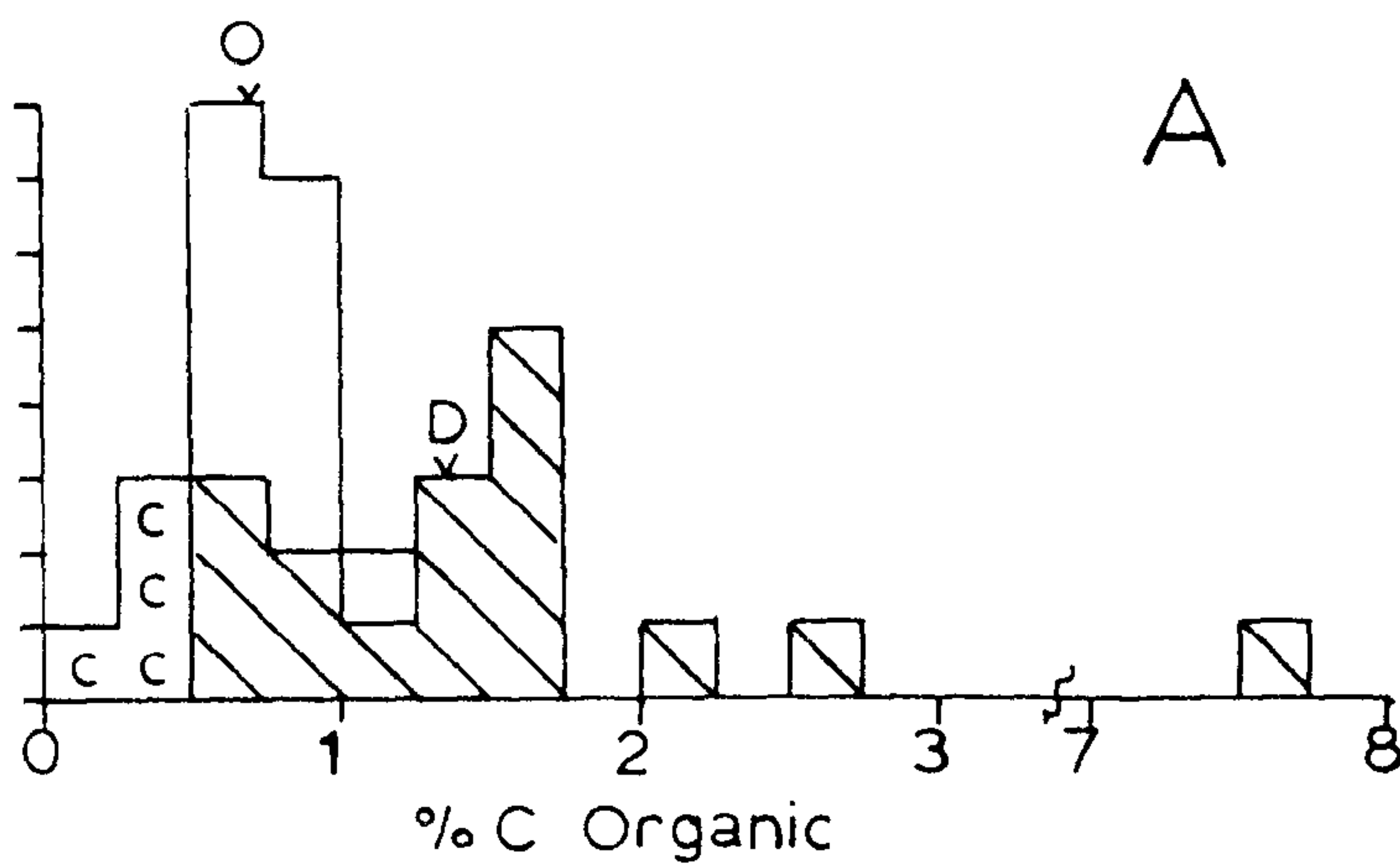


Fig 1. Histogram of Data from the Upper Oxford Clay

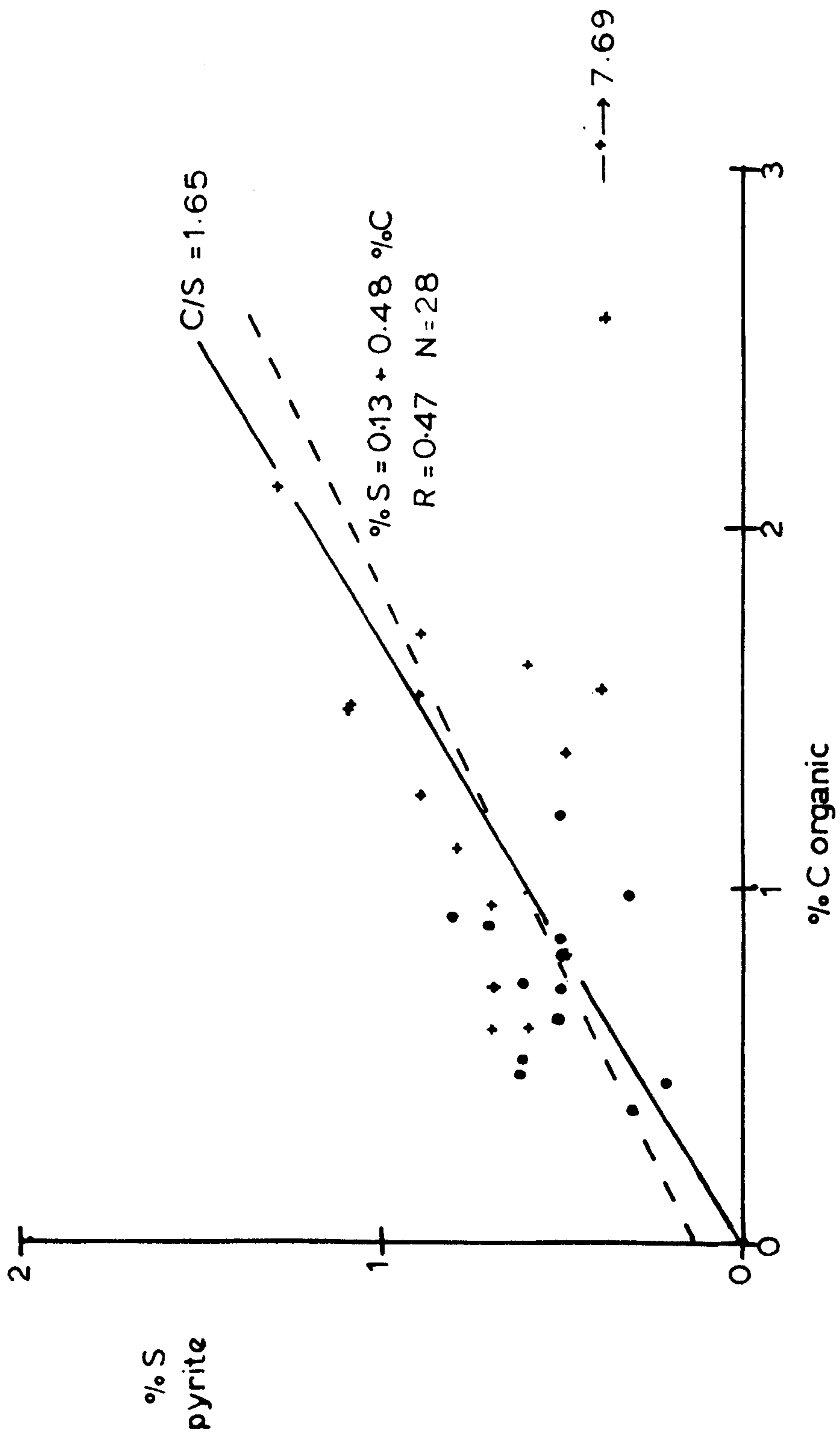
(plain squares) and the Dunans Clay (hatched sq) cementstone horizons in the U.O.C are indicated by Cs. Os and Ds indicate the means for the two clays on each plot. A. Organic Carbon  $O=0.70$ ,  $S=0.27$ ;  $D=1.35$ ,  $S=0.55$ . B Carbonate Carbon  $O=3.65$ ,  $S=0.47$  (Cementstones excluded);  $D=2.34$ ,  $S=0.92$ . C Pyrite Sulphur  $O=0.51$ ,  $S=0.17$ ;  $D=0.72$ ,  $S=0.26$ . D HCl Soluble Iron  $O=1.08$ ,  $S=0.17$ ;  $D=1.59$ ,  $S=0.42$ . E S34S  $O=-36.9$ ,  $S=3.44$ ;  $D=-36.0$ ,  $S=7.20$ . F Degree of





**Fig 4. Plot of  $\delta S$  pyrite vs  $\delta C$  organic carbon.**

**• Upper Oxford Clay, + Dunans Clay**



# The Relationship Of Environment of Deposition To the Formation of Sedimentary Pyrite in the Lower Oxford Clay (Callovian) England

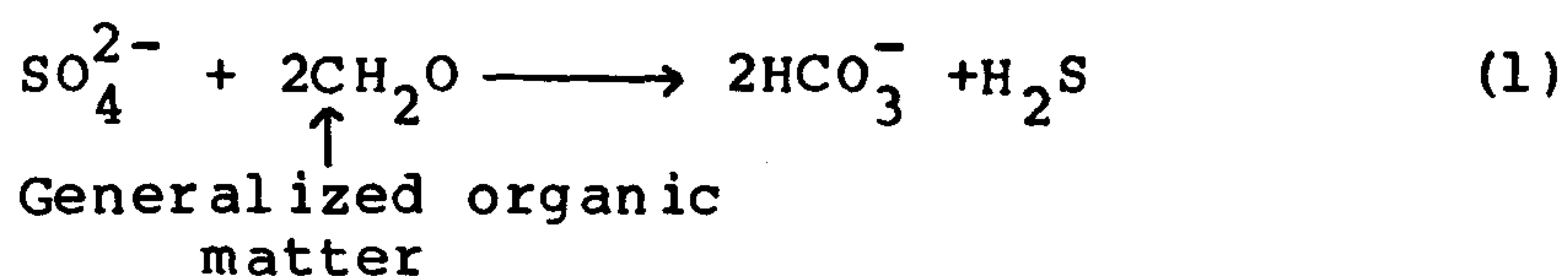
## 1. Introduction.

In recent years many studies have been made of sulphate reduction in recent anoxic muds, and the associated isotope variations (eg. Berner 1978,1980; Goldhaber & Kaplan 1974,1980; Goldhaber et al 1977; Chambers 1982), but little work has been done on the ancient counterparts of these muds. Hudson (1982) published the results of a petrographic study of pyrite in various Jurassic shales. The small amount of work undertaken on ancient sediments has revealed a wide range of sulphur isotope values (Coleman & Hudson 1980). Some variations can be ascribed to different generations and phases of pyritization and the relative availability of organic matter and sulphate. These factors do not totally explain the ranges found. In this study it was intended to investigate in more detail the variation in pyrite content and its sulphur isotope composition, and to see how these related to the factors which are thought to control them in recent sediments, ie. organic carbon content, availability of sulphate and iron, rates of sedimentation and bottom water conditions. Consequently samples of the Lower Oxford Clay were

examined as an example of a particular shale environment, for which good control on the bottom water conditions is available from the palaeoecological work of Duff (1975). Samples of shale were analysed for the sulphur isotopic composition of the fine-grained pyrite, organic and carbonate carbon content and HCl soluble iron. As well as the shale samples examples of pyritized fossils and concretions were examined ; detailed petrographic descriptions are presented elsewhere (chapter 6).

## 2. Factor Affecting Pyrite Formation.

The formation of pyrite in marine sediments is due to the action of sulphate-reducing bacteria on seawater sulphate to form sulphide, which reacts with iron to form pyrite, either directly or via a monosulphide phase (Goldhaber and Kaplan 1974). The reactions may be summarized thus:-



The formation of pyrite requires four prerequisites,

1. Anoxic conditions in which the bacteria can live.



2. sulphate.
3. Organic matter on which the bacteria may feed.
4. Iron to precipitate the sulphide formed by bacterial action.

Sulphate-reducing bacteria are obligate anaerobes and therefore require oxygen-free conditions in which to live. This requirement is served equally well by a totally anoxic sediment or water, or by an anoxic micro-environment within otherwise oxic conditions.

Sulphate is required as the sulphur source but does not affect the formation unless below 2mmolar (Rees 1975). The sulphate in solution may enter the surface layers of the sediment due to mixing by burrowing organisms, or by turbulence in the bottom waters. It reaches deeper layers within the sediment by diffusion, the gradients controlled by the rate of sulphate reduction (Berner 1980).

Various laboratory cultures of sulphate-reducing bacteria indicate that the rate of sulphate reduction is dependent on both the quantity and quality of organic matter (Harrison and Thode 1958, Kaplan and Rittenberg 1964). A general covariance between the concentration of organic matter and the pyrite content has been observed by various authors (Berner 1970, Sweeney 1972, Goldhaber

and Kaplan 1974). This is ascribed to the greater initial concentrations of organic matter giving rise to more pyrite formation, which, if the proportion of organic matter being utilized during sulphate reduction is a constant proportion of the total organic matter entering the sulphate reduction zone, will result in a linear correlation between organic carbon and pyrite sulphur. For constant proportion of organic matter to be used during sulphate reduction the organic matter entering the sediment must be of a more or less constant composition from one area of deposition to the next. The composition of organic matter entering the sulphate reduction zone depends strongly on the environment through which it has passed. The organic matter entering the sulphate reduction zone will have been acted on by aerobic bacteria (Curtis 1977), which not only decreases the total organic matter, but preferentially removes the short chain carboxylic acids (Zolnay 1971), which are the favoured food of the sulphate-reducers. Therefore the more limited the the aerobic zone of bacterial reduction the more total and metabolisable organic matter will enter the sulphate reduction zone.

The presence of ferrous iron is necessary for the precipitation of any sulphide produced. If iron is not present in a suitable form then the sulphide may be lost from the system and re-oxidised, or react with other

substance or organic matter. A measure of the availability of iron was devised by Berner (1970), who found that the reactivity of minerals such as hematite, limonite, goethite, chlorite, hornblende, augite and biotite to  $H_2S$  is similar to that with hot HCl. Therefore the values of HCl soluble iron (%FeHCl) represent the amount of iron in a sediment, which could have formed pyrite had sufficient  $H_2S$  been present. The value of %FeHCl should probably be considered as a maximum as the high concentration of HCl used in the test solubilizes a larger quantity of iron than would have reacted at the relatively low concentrations of  $H_2S$  in sediments. A useful measure is that of the degree of pyritization, (D.O.P.) which is defined as,

$$D.O.P. = \frac{\%Fe \text{ as pyrite}}{\%Fe \text{ as pyrite} + \%FeHCl} \quad (3)$$

This is a measure of the amount of originally available iron which has formed pyrite, and has a value between 0 and 1. If iron is limited then the value will approach 1, but as %FeHCl represents a maximum it will probably never reach it.

### 3. Causes of Sulphur Isotopic Variation.

The isotopic variations associated with the bacterial reduction of sulphate have been experimentally

investigated by several authors (a good review is given by Chambers and Trudinger 1979). Experiments have revealed isotopic effects between +3 and -46‰ which are directly related to the specific rate of sulphate reduction (Chapter 1). It has been suggested that at extremely slow rates of reduction fractionations may approach equilibrium values of -74‰ at 25°C (Tudge & Thode 1950, Trudinger & Chambers 1973).

A compilation of fractionation factors for sulphate reduction in recent sediments given by Chambers and Trudinger (1979) ranges between -34‰ and -59‰ with a mean about -50‰, which exceeds the largest fractionation found by experiment. This may be an effect of extremely slow rates of sulphate reduction in natural sediments or possibly of the reoxidation of light sulphide in the surface layers of the sediment lowering the isotopic composition of sulphate (Chapters 1 & 2).

As well as the variation in the isotopic fractionation, the so-called reservoir effect must be taken into account when considering the final isotopic composition of pyrite. This occurs when the sulphate is not replenished in the system and so becomes progressively heavier due to the preferential removal of lighter sulphide. This will result in the sulphide produced becoming progressively heavier, a process similar to Rayleigh distillation.

The final composition of fine-grained pyrite will eventually be a mixture between pyrite formed within the "open system", in a zone of bioturbation and mixing , and that formed within a partially closed system where sulphate is supplied by diffusion (Goldhaber & Kaplan 1980). Goldhaber assumed that the sulphide formed within the zone of bioturbation had an isotopic composition 45‰ lighter than seawater sulphate. Sulphide formed from sulphate diffusing into the sediment would, on complete reduction, equal about seawater-25‰. A small amount of sulphide would be contributed from the sulphate trapped in the sediment on burial; this would yield sulphide at seawater values. Goldhaber and Kaplan demonstrated that the isotopic composition of sulphide in the sediments of the Gulf of California could be explained by summing the isotopic values in proportion to the amounts of pyrite formed in each zone. The values assume complete reduction and trapping of sulphate; this will only occur when the sulphate reduction is limited by sulphate diffusion (as in the Gulf of California sediments) and when there is sufficient iron to trap all the sulphide formed. If the sulphate reduction is limited by organic carbon not all sulphate will be reduced and the resulting isotopic values will be more negative than those predicted by the Goldhaber and Kaplan model.



### 4. The Lower Oxford Clay.

The sections of the Lower Oxford Clay sampled for this study were exposed at the London Brick Company pits at Peterborough (Norman Cross pit), Stewartby, Bedfordshire, and Bletchly and Calvert, Buckinghamshire (fig 1). The Lower Oxford Clay occupies the upper part of the Lower Callovian, the Middle , and the lower part of the Upper Callovian. It is bounded at its base by the Kellaways sands and overlain by the paler less bituminous Middle & Upper Oxford Clay.

4.1. Lithology: The Lower Oxford Clay is a sequence of bituminous shales ranging in colour from Olive Gray (5Y4/1) to Light Olive Gray (5Y6/1) when dry (American Geological Institute Rock Colour Chart). The Carbonate content of the shales varies from 0.13-4% carbonate carbon. Its organic carbon content is relatively high between 2 and 11% organic carbon and averaging about 5%. It is its high organic carbon content which makes it uniquely suitable for the manufacture of bricks using the Fletton process. The sequence is broken at several layers by concretions, described by Hudson (1978), and by various shell beds (Duff 1974,1975).

4.2. Palaeoenvironments: The Lower Oxford Clay is

Classified by Morris (1980) as a "Restricted" shale, in his tripartite division of mudrocks. It can be viewed as a fine-grained sediment deposited in a shallow shelf sea with little agitation below wave base allowing the development of poorly oxygenated bottom waters (Hallam 1975). The oxic/anoxic boundary lay a few centimetres below the sediment water interface. This allowed the presence of tolerant deposit feeders, and various epifaunal suspension feeders which lived removed from the bottom, possibly suspended from floating wood or weeds; Duff (1975) termed these pendent bivalves. Within the Lower Oxford Clay Duff has identified 10 biofacies subdivided on the lithology and faunal content. These biofacies represent variations in the general environment and changing oxygen levels in the bottom waters.

4.3 Biofacies: A distribution of the biofacies at the four pits is given on fig 2, which also indicates sampling points in the sections. Below is given a brief description of the biofacies and the environmental variations they represent.

a) Silts and Silty Clays. These are part of the transgressive sequence from the Kellaways sands to the Oxford Clay. Good aeration of the bottom waters allowed a diverse fauna of infaunal and epifaunal suspension

feeders.

b) Bituminous Shales.

- Deposit feeder bituminous shales. These are believed to be the least well aerated of the bituminous shales the fauna is dominated by pendent bivalves with a benthic fauna of deposit feeding bivalves and gastropods.
- Grammatodon-rich bituminous shales. Dominated by infaunal suspension feeders are believed to be better oxygenated than the deposit feeder shales.
- Foram-rich bituminous shales. The degree of bottom water oxygenation probably lay somewhere between that of the deposit feeder and the Grammatodon-rich shales, they are distinguished by the presence of abundant forams.

c) Shell Beds.

The shell beds are probably formed as concentrations of shells in situ due to the increased current activity winnowing fine grained material from the shells. They contain faunas similar to the shales in which they occur:

Nuculacean shell beds in deposit feeder bituminous shales,

Meleagrinella shell beds in the calcareous clays (Q.V.),

Grammatodon shell beds in the Grammatodon-rich shales,

Gryphea shell beds in the silts and silty clays.

The Gryphea shell beds show evidence for movement of shells with disarticulated and fragmented shells, broken cephalopods and worn bone.

### d) Calcareous Clays.

These are found alternating with the Meleagrinnella shell beds in the upper portion of the sequence. They contain an almost equal distribution of deposit and suspension feeders. They probably represent the most oxygenated, non shell bed biofacies of the Lower Oxford Clay, but appear not to have reached the degrees of oxygenation of the Middle and Upper Oxford Clay.

### e) Blocky Claystone.

This is known only from the jason subzone at Calvert; occurring within deposit feeder bituminous shales. It is dominated by pendent bivalves but Lingula and Solomya (both tolerant of low oxygen conditions) are characteristic. The horizon may represent a local occurrence of very poorly oxygenated water.

4.4. Occurrence of Pyrite: Pyrite occurs in several forms and situations within the Lower Oxford Clay. It is found as fine-grained disseminated pyrite in the form of 5 to 15µm framboids. Pyrite is associated with various fossils, replacing mollusc shells and wood , as infillings in bone and as coatings on belemnite guards.

It occurs in concretions, which are often associated with flattened macroconch ammonites, and as localized occurrences in shell beds, most noticeably the Basal Pyrite Shell Bed at Calvert and the Mid-grossouvrei shell bed at Stewartby. Small irregular pyrite nodules 5-10cm max diameter have been found in the Peterborough district but the horizon of their occurrence is unknown. Some larger pyrite nodules have been found associated with vertebrate material at Milton Keynes (D.M.Martill, pers comm). Pyrite is also found as the lining to septaria in carbonate concretions (Hudson 1978).

For the purposes of this study three distinct occurrences of pyrite have been studied.

- 1) Fine-grained pyrite in the shales.
- 2) Shell replacement pyrite in small bivalves and ammonites from shell beds.
- 3) Concretionary and replacement pyrite associated with macroconch ammonites.

Fig 2 shows the positions of shale samples and fig 3 shows the sampling from ammonite concretions.

### 5. Experimental Techniques and Results.

5.1. Techniques: Samples of shale were either crushed and ground in a Tema Mill or drilled from hand specimens using a jewellers drill. Samples of the pyrite from



concretions were drilled from polished blocks. Small shells were separated from the shell beds by washing and sieving. Samples of the shale matrix was extracted separately by drilling so that the isotopic composition of the fine-grained pyrite in the shell beds could be analysed.

Samples of shale were analysed for organic and carbonate carbon using a two stage wet chemical technique, a modification of that of Bush (1970), where carbonate-carbon is liberated as carbon dioxide by the action of Analar phosphoric acid. The carbon dioxide is reacted with a known quantity of standard barium hydroxide, which is then back-titrated with standard hydrochloric acid. The sample mixture is then reacted with saturated chromic acid and again the carbon dioxide formed is trapped in barium hydroxide.

Shale samples were also analysed for hydrochloric acid soluble iron (%FeHCl). A method similar to that of Berner (1970) was employed. 0.2g of powdered sample was boiled for 2min with 3ml of concentrated analar hydrochloric acid. The liquid was diluted to 10ml and analysed on a Perkin Elmer Atomic Absorption Spectrometer.

Sulphur for isotopic analysis was extracted as sulphur dioxide at high temperature using cuprous oxide

(Robinson and Kusakabe, 1975) using an extraction line set up as described by Coleman and Moore (1978). It was found necessary to pretreat shale samples with 10% acetic acid to remove carbonate and to react them for 12hrs in an oxygen plasma using a Nanotech Pl00 Plasmaprep, a low temperature ashing furnace, to remove any organic matter present. Both the carbonate and organic carbon would react during sulphur extraction and yield carbon dioxide which, when present in large quantities, interferes with the extraction. The removal of organic matter by oxygen plasma should serve to rid the sample of any organic sulphur present. Both treatments with the acid and the oxygen plasma were undertaken quantitatively so that the yield of sulphur dioxide obtained during sulphur extraction could be used as a measure of the pyrite sulphur content of the shale. The sulphur dioxide was analysed on a micromass 602-C mass spectrometer with heated inlet. Raw data were corrected for instrumental and isobaric effects (Coleman 1980). The results are presented in tables 1 & 2. The analytical precision for sulphur isotope analyses is 0.05‰. The reproducibility of results on shales though is about 0.7‰. The reproducibility of %organic and carbonate carbon are 0.1% and for pyrite sulphur less than 0.14%. Iron determination are of the order of 0.1%.

5.2.Results: The raw data from table 1 and 2 are presented as histograms figs 4 & 5. The first four histograms show data from the shale and clay biofacies only, the fifth all the isotopic data obtained from the Oxford Clay. The results for  $\delta^{13}\text{C}_{\text{org}}$  are presented as straight values and in terms of the ratio D.O.P.

5.3. Variation of Organic Carbon, Carbonate Carbon, Pyrite Content and  $\delta^{34}\text{S}$  in Shale and Clay biofacies:

From the data on the organic and carbonate carbon and the pyrite content it is possible to characterize each of the five shale and clay biofacies on a unique combination of the three parameters i.e.

Deposit feeder bituminous shales have a higher pyrite sulphur content than the other shales and clays except the blocky claystone. The foram-rich bituminous shales have a significantly higher organic carbon content; the calcareous clays, as their name suggests, a higher carbonate content. The Grammatodon-rich bituminous shales are distinguished by not having any of the notable characteristics of the other biofacies, or any significantly low values. The blocky claystone, although only one sample was analysed, shows extreme values for each of the parameters; highest pyrite content, lowest carbonate and organic carbon contents.

These variations confirm that Duff's (1975) biofacies do

represent real variation in the chemical parameters. . Although the samples can be divided between the biofacies by a combination of the above parameters, their appears to be no significant distinction in the  $\delta^{34}\text{S}$  means and ranges.

The  $\delta^{34}\text{S}$  values range between  $-28\text{‰}$  and  $-10\text{‰}$  with a mean of  $-21.5\text{‰}$  and all the shale and clay biofacies spread across this range.

#### 5.4. Hydrochloric Acid Soluble Iron and Degree of

Pyritization: The Hydrochloric acid soluble iron is a measure of the the amount of iron , which is present in the sediment, and would have formed pyrite if sufficient hydrogen sulphide had been produced. The value of  $\% \text{FeHCl}$  represents the maximum amount of iron still remaining which could have formed pyrite. As the values for  $\% \text{FeHCl}$  are maxima the values of D.O.P. represent minima. The  $\% \text{FeHCl}$  values for the Lower Oxford Clay as a whole are fairly high compared to other shale (see chapters 2 & 4). The values of D.O.P. for the Lower Oxford Clay which lie below 0.71 do not suggest that iron was a limiting factor in the formation of pyrite. The formation of pyrite in the Lower Oxford Clay was therefore limited by either the diffusion of sulphate or the concentration of metabolisable organic matter.

5.5. variations of  $\delta^{34}\text{S}$  for all samples: The overall spread of  $\delta^{34}\text{S}$  values is between -28 and +40‰. They can though be divided into four significantly different groups.

- 1) Fine-grained pyrite in the shales -28 to -11‰  
mean -21.5‰
- 2) Fine-grained pyrite in shales -24 to +7‰  
matrix of Shell beds mean -15.7‰
- 3) Small pyrite-replaced shells  
from shell beds -8‰ to +18‰  
mean +7.2‰
- 4) Concretionary and shell  
replacement pyrite from  
ammonite concretions +10‰ to +40‰  
mean +26‰

## 6. Discussion of Results.

6.1. Variations within Shale and Clay Biofacies: As indicated above the sulphur isotope composition does not appear to depend on biofacies. The pyrite content does appear to be partially related to biofaces with the least oxygenated biofacies having the most pyrite and vice versa. What then produces the variation of  $\delta^{34}\text{S}$  values? The  $\delta^{34}\text{S}$  value does not appear to be directly



related to,

- 1) The Pyrite Content.
- 2) Organic Carbon Content.
- 3) Carbonate Content.
- 4) Biofacies.
- 5) Mean Sedimentation Rate.

If the average sedimentation rate is calculated at each pit for each subzone, and compared against the mean  $\delta^{34}\text{S}$  values for the subzone, no correlation is seen.

For the values of fine-grained pyrite, we can consider that the final pyrite consists of pyrite formed within the top few centimetres of the sediment where bioturbation and mixing occur, together with pyrite formed in a zone where sulphate is supplied by diffusion (Goldhaber and Kaplan 1980). In the former pyrite may have formed at 45‰ less than Jurassic seawater (+16‰ Claypool et al, 1980) giving a value of -29‰ (but if we follow Chambers and Trudinger, 1979 the value will be nearer -34‰ using a fractionation of -50‰). In the case of the zone of diffusion pyrite forms at seawater-25‰ (= -9‰) with a small component at +16‰ from sulphate trapped in the sediment.

A simple calculation may be performed to find the the average isotopic composition of the Lower Oxford Clay pyrite. The amount of pyrite formed in the zone of diffusion is limited by the diffusivity of the sediment and the concentration of sulphate in the seawater. From

the solutions of the general steady state diagenetic equations given by Berner (1980),

$$C = \frac{W^2 \cdot F \cdot L \cdot G_o \cdot \exp((-K/W)X)}{W^2 + K \cdot D_s} + C_\infty \quad (4)$$

$$G = G_o \cdot \exp((-K/W)X) \quad (5)$$

$$C_o - C_\infty = \frac{W^2 \cdot F \cdot L \cdot G_o}{W^2 + K \cdot D_s} \quad (6)$$

$$\Sigma S = L \cdot F \cdot G_o [1 - \exp(-K/W)X] \quad (7)$$

C = concentration of sulphate in pore water ( $\mu\text{moles/ml}$ )

$C_o$  &  $C_\infty$  = initial and final concentrations of sulphate

W = sedimentation rate

K = first order rate constant for organic degradation.

G = concentration of metabolisable organic matter ( $\mu\text{moles/g}$ )

$G_o$  &  $G_\infty$  = initial and final concentrations of organic matter.

L = The stoichiometric coefficient, moles of sulphate reduced/moles of organic matter oxidized to  $\text{CO}_2$ .

F =  $(1+\phi) \cdot \rho/\phi$  and is the concentration conversion factor where  $\phi$  is the porosity and  $\rho$  the density of the sediment.

$\Sigma S$  = total reduced sulphide.

$D_s$  = the diffusivity of the sediment.

If we substitute for K using the Toth and Lerman (1977)

equation  $K = AW^2$ , where A is an empirical constant then

when  $C \rightarrow 0$   $\Sigma S = C_o(1 + A \cdot D_s)$ . Using general values for

$A = 0.04 \text{ yr/cm}^2$ ,  $D_s = 100 \text{ cm}^2/\text{yr}$ ,  $C_o = 28 \mu\text{moles/ml}$

then  $\Sigma S = 140 \mu\text{moles/ml}$  or approx 0.6% pyrite sulphur.

The average pyrite sulphur content of the Lower Oxford clay is 1.4%, therefore, assuming that sulphate is limiting pyrite formation, the other 0.8‰ is formed in the zone of bioturbation. Assuming that pyrite forms with an isotopic value of -34‰ in the zone of mixing

and -9‰ in the zone of diffusion then the average  $^{34}\text{S}$  value for pyrite in the Lower Oxford Clay should be

$$\frac{0.6 \times (-9) + 0.8 \times (-34)}{1.4} = -23.3\text{‰} \quad (8)$$

This is slightly more negative than the real mean -21.5‰, but extremely close. If allowance is made for the pyrite formed from sulphate trapped in the sediment at +16‰, it can be assumed that 0.1‰ of the total sulphur formed in that way, then the resulting isotopic sum becomes -19.7‰. The relative closeness of these values would suggest that the Goldhaber and Kaplan type model with sulphate as the limiting factor in pyrite formation is applicable to the Lower Oxford Clay. The variations of isotopic composition will depend on the relative proportion of pyrite formed in the "open" and "closed" system. This could be achieved by variations from the steady state model, eg. due to small changes in sedimentation rate.

When plotted on a S vs C plot (Fig 6) the data from the Lower Oxford Clay do not show the expected positive correlation as suggested by Sweeney (1972). If sulphate reduction in the Lower Oxford Clay is limited by sulphate diffusion, then excess organic matter will be able to pass through the sulphate reduction zone so yielding higher than expected C/S ratio for the samples

with initially high organic input. This though does not explain the weak negative trend found on fig 6. The weak negative trend is probably explained by variations in the organic productivity and the oxygenation of the bottom water. In the more oxic conditions the organic matter is subject to more aerobic degradation, hence the organic matter entering the sediment is more refractory. In the case of the foram-rich bituminous shales, although the initial productivity of organic matter was greater, the more oxic condition led to a smaller proportion of metabolisable organic matter entering the sediment and so a higher C/S ratio. The opposite is the case for the blocky claystone. In the case of the deposit feeder and Grammatodon-rich bituminous shales, which have similar organic carbon contents, the more oxic Grammatodon-rich shale has the lower pyrite content.

## 6.2 Isotopic Variation in Shell Replacement and

Associated Concretionary Pyrite: The pyrite in shells and ammonite concretions may be divided into two phases, 1) Pre-crushing in or just below the zone of mixing with isotopic values upto +18‰.

2) Post-crushing: further replacement of shell and formation of concretionary pyrite upto +40‰.

These two subdivisions are in agreement with the petrographic evidence (Chapter 6). The small shells from the shell beds show original microstructure faithfully



replaced by pyrite. This appears to have occurred prior to crushing. Some shells contain relict carbonate in centres of the shells, indicating that sulphate supply was probably initially by diffusion. The earliest replacements are of the organic matrix of the shell with little or no solution of the aragonite. There are three explanations for the  $\delta^{34}\text{S}$  values (-8 to +18‰) which are considerably heavier than the fine-grained pyrite.

1. The earliest formed hydrogen sulphide was lost from the shell and so the  $\delta^{34}\text{S}$  values correspond to pyrite formed deeper in the sediment where sulphate had become enriched.

2. The shells represent a partially closed system where sulphate is supplied by diffusion.

3. The fractionation factor for sulphate reduction occurring in the shells is smaller than that for reduction occurring in the sediment.

There is evidence to support all these hypotheses. Within the shell, where sulphate reduction is occurring iron is limited and must be supplied by diffusion from outside. If during the earliest stages of sulphate reduction the surrounding sediment is aerobic, iron will be in the ferric form and unable to diffuse, hence the earliest formed sulphide may be lost. This hypothesis is supported by the limited solution of aragonite at the early stages of replacement. Coleman & Raiswell (in press) have demonstrated that a balance exists between



pyrite precipitation and carbonate solution. When iron is present hydrogen sulphide is precipitated as pyrite or another iron sulphide, and protons are liberated which can dissolve preexisting carbonate. If iron is not present the hydration of the sulphide ions leads to the release of hydroxyl ions, which can lead to the precipitation of carbonate. The lack of solution would suggest a limitation of iron. The presence of aragonite relics in the central parts of shells suggests that sulphate was limited by diffusion. Early replacements in ammonites show an ovoid texture which is interpreted as resulting from the effects of diffusion (Chapter 6). This may have resulted in the formation of a partially closed system in the shell with continuous reduction leading to more positive  $\delta^{34}\text{S}$  values. The maximum  $\delta^{34}\text{S}$  values for pyrite achieved upon total reduction of sulphate entering the shell will be  $< \delta^{34}\text{S}$  value of external pore water sulphate. The maximum value of +18‰ for the small shells suggest pyrite formation early in the sediment before the porewater sulphate became significantly enriched. The initial sulphate reduction appears to have occurred with the organic matrix of the shell as substrate. The richness of the substrate may have lead to rapid sulphate reduction and hence lower fractionations. These three possibilities are not mutually exclusive and the real picture may be a combination of all three.

The pyrite formed in the heavily overpyritized ammonite concretions shows textures and isotopic compositions consistent with the formation of a large portion of the pyrite late in the zone of diffusion after the crushing of the ammonites, when pore water sulphate had become depleted. On crushing the interiors of the shells were open to sulphate and iron-rich solutions. The later phases yielded  $\delta^{34}\text{S}$  values up to +26‰. When sampling the concretion OCC81/L2 across its thickness, it was found that the interior of the concretion had a heavier isotopic composition. This may suggest that the outer pyrite formed earlier.

In Fig (7) a summary of the times, depth and isotopic values of pyrite formation is attempted.

### 6.3. Fine-Grained Pyrite from the Shale Matrix of Shell

Beds: These samples showed distinctly heavier  $\delta^{34}\text{S}$  values compared to the fine-grained pyrite from shales. On examination of the pyrite by scanning electron microscopy it was found that the samples contained fragments of pyritized shell and foraminifera. The isotopic values for the shale matrix from shell beds represents a mixture of the general fine-grained dispersed pyrite with the heavier early shell replacement pyrite and, in the case of the extreme +7‰ value some later concretionary pyrite.

## 7. Conclusions

1. The formation of pyrite in the Lower Oxford Clay was primarily limited by the diffusion of sulphate.
2. It is seen to be related to the oxygenation of the bottom waters. This has affected the amount and composition of organic matter entering the sulphate reduction zone. The least oxygenated biofacies allow a larger proportion of the more metabolisable fractions to enter the zone. The better oxygenated facies, even where the organic productivity was higher, yield lower than expected pyrite sulphur contents as the proportion of metabolisable organic matter has been reduced due to effects of aerobic oxidation.
3. The isotopic composition of fine-grained pyrite lies between -44‰ and -27.5‰ less than seawater sulphate, and is not primarily dependent on the following:
  - a) Pyrite content
  - b) Organic carbon content
  - c) Biofacies
  - d) Average sedimentation rate

The formation of the pyrite can be viewed as occurring within two zones.

- a) A zone of bioturbation and mixing with pyrite forming at seawater-50‰.
- b) A zone of diffusion where on total reduction of sulphate the pyrite formed has an isotopic composition

of seawater-25‰ with a smaller amount of sulphide formed from sulphate trapped on burial with a value of +16‰ (seawater).

The overall isotopic composition is dependent on the proportions of pyrite formed in each zone. The amount of pyrite formed in the zone of diffusion under steady state conditions is limited by the diffusivity of the sediment and the concentration of sulphate in the seawater. The relative proportions of pyrite formed in the zones are therefore altered by variation in the amounts formed in the zone of mixing and by non-steady state variations in such parameters as rate of sedimentation.

4. Shell replacement pyrite forms within the sediment with associated pyrite concretions. The formation commences early during burial and continues after the crushing to depths where sulphate is significantly enriched in  $^{34}\text{S}$ . Two main phases of replacement are seen to correspond with the isotopic values.

- a) Pre-crushing values up to +18‰
- b) Post-crushing values up to +40‰ with associated concretionary pyrite.

5. The shell replacement and concretionary pyrites are noticeably heavier than the fine grained dispersed pyrite. The effects of mixing the two kinds is found in the shell beds.

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- Fig 4 & 5 Histograms of data from Lower Oxford Clay. Deposit feeder shales plain squares; Foram-rich shale f; Grammatodon shales g. Calcareous clays c; Blocky claystone b. Capital letters indicate means of data for each biofaces, D indicate deposit feeder shales. 4A Carbonate carbon



G=0.97,  $\delta$ =0.60; D=1.00,  $\delta$ =0.66; F=1.38,  $\delta$ =0.85;  
C=3.01,  $\delta$ =1.13. 4B Organic carbon C=4.44,  $\delta$ =1.08;  
G=4.58,  $\delta$ =1.59; D=4.79,  $\delta$ =1.68; F=7.19,  $\delta$ =1.65.  
5A Pyrite sulphur D=1.45,  $\delta$ =0.22; C=1.15,  $\delta$ =0.29;  
G=1.125,  $\delta$ =0.27; F=1.057,  $\delta$ =0.22.

Fig 5B gives all the isotope data for the Lower Oxford Clay. V indicate means of various groups for data, see text.

Fig 6. Plot of Pyrite sulphur content Vs Organic Carbon Content.

Fig 7. Summary of supposed variations of sulphur content and  $\delta^{34}\text{S}$  values for porewater sulphate and fine-grained pyrite with depth, and the stages of replacement of shells and associated concretionary pyrite formation.

Table 1a  
DATA FOR LOWER OXFORD CLAY

SAMPLE	TYPE	%S Pyrite	δ34S	%C Organic	%C Carb- onate
Norman Cross Brickpit					
OCN81/1	NSB	1.0	-17.0	N.D	N.D
OCN81/2	D	1.5	-13.9	4.23	0.95
OCN81/3A	D	1.5	-13.5	4.49	1.05
OCN81/3B	D	1.3	-23.5	4.92	2.50
OCN81/4	D	1.0	-22.8	4.52	2.36
OCN81/5	NSB	2.3	-19.9	N.D	N.D
OCN81/6	D	1.5	-12.0	4.27	1.51
OCN81/7	D	1.5	-16.3	4.57	1.37
OCN81/8	G	1.2	-13.7	3.60	1.60
OCN81/9	G	1.5	-19.1	3.18	1.68
OCN81/10	F	0.9	-22.6	8.02	0.55
OCN81/11	MSB	3.4	-17.0	6.71	1.04
OCN81/12	D	1.4	-25.2	10.40	1.88
OCN81/13	GRSB	1.3	-20.7	N.D	N.D
OCN81/14	D	1.4	-25.7	9.44	2.22
OCN81/15	GRSB	1.6	-23.5	N.D	N.D
OCN81/16	D	1.6	-20.5	N.D	N.D
Stewartby Brickpit					
OCS81/1C	NSB	1.2	-14.2	N.D	N.D
OCS81/2D	NSB	0.9	-17.1	N.D	N.D
OCS81/3	MSB	1.3	-19.6	2.72	2.73
OCS81/5A	F	1.1	-18.9	4.74	1.12
OCS81/5B	GSB	0.7	-8.8	3.41	1.46
OCS81/7	G	1.4	-11.5	4.69	0.68
OCS81/8	G	0.7	-13.9	4.31	1.14
OCS81/9B	MSB	6.2	+6.8	N.D	N.D
OCS81/10	F	0.8	-13.3	5.41	1.33
OCS81/11	C	1.4	-20.0	3.60	1.73
OCS81/12	C	0.9	-18.7	3.49	3.88
OCS81/15	D	1.0	-16.0	3.62	0.71
OCS81/16	NSB	1.2	-18.6	N.D	N.D
OCS81/18	D	1.3	-20.9	3.80	0.44
OCS81/19	D	1.2	-24.2	4.47	0.80
OCS81/20	D	1.9	-18.1	5.06	0.76
OCS81/21	D	1.7	-13.5	5.17	0.93
Calvert Brickpit					
OCC81/1	D	1.6	-16.8	5.54	1.30
OCC81/3A	NSB	1.7	-17.1	7.59	0.35
OCC81/4	G	0.9	-22.6	4.82	0.35
OCC81/5	G	0.9	-24.0	N.D	N.D
OCC81/6	F	0.7	-22.7	9.44	1.86
OCC81/8A	GRSB	1.2	-21.3	N.D	N.D
OCC81/7	F	1.0	-23.7	8.40	0.47
OCC81/9	C	1.4	-25.3	4.98	N.D

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SAMPLE	TYPE	Table 1a			
		%S Pyrite	$\delta^{34}\text{S}$	%C Organic	%C Carb- onate
OCC81/10	MSB	0.9	-19.4	N.D	N.D
OCC81/11	NSB	1.7	-13.0	N.D	N.D
OCC81/14A	D	1.2	-24.2	4.60	0.13
OCC81/15	D	1.5	-27.8	2.54	0.42
OCCS1/16	D	1.6	-22.5	4.59	0.23
OCC81/17	B	1.9	-27.8	2.05	0.16

Bletchley Brickpit

OCB81/1	F	1.1	-24.6	7.74	2.65
OCB81/2	C	0.9	-24.6	5.70	3.42
OCB81/4	F	1.4	-26.4	6.37	0.66
OCB81/5	F	1.2	-21.3	7.68	2.43
OCB81/6B	G	1.2	-23.3	6.86	0.36
OCB81/8	D	1.4	-21.9	5.04	1.16
OCB81/9	D	1.3	-23.9	4.39	0.69
OCB81/10	D	1.9	-25.4	4.61	0.36
OCB81/11	D	1.5	-19.8	4.71	0.79
OCB81/12	D	1.6	-21.3	3.90	0.76
OCB81/13	D	1.3	-23.9	3.61	0.77
OCB81/14	D	1.5	-25.4	3.32	0.71
OCB81/15	D	N.D	N.D	3.95	0.26

Shale Types. D=deposit feeder shales. F=foram-rich shales. G=Grammatodon-rich shales. C=calcareous clays. B=blocky claystone. NSB=Nucula shell bed. MSB=Meleagrinnella shell bed. GSB=Grammatodon shell bed. GRSB=Gryphea shell bed

Table 1b

Acid Soluble Iron Data  
Sample            %Fe            D.O.P.

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OCN81/7	0.68	0.66
OCN81/8	0.67	0.61
OCN81/9	0.56	0.71
OCN81/10	0.62	0.56
OCN81/12	1.33	0.48
OCS81/20	0.69	0.71
OCC81/4	0.67	0.54
OCC81/6	0.61	0.50
OCC81/7	0.68	0.56
OCC81/15	0.82	0.62
OCB81/1	0.69	0.58
OCB81/2	0.67	0.54
OCB81/4	0.74	0.62
OCB81/5	0.74	0.59
OCB81/6B	0.79	0.57
OCB81/9	0.74	0.61
OCB81/10	0.81	0.67
OCB81/11	0.81	0.62
OCB81/12	0.96	0.59
OCB81/13	0.85	0.57
OCB81/14	0.82	0.62

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Table 2  
34S Values For Pyrite Replaced Shells And Associated  
Concretionary Pyrite

Small Pyrite Replaced Shells From Shell Beds

Sample	Shell Type	δ34S CDT
OCS 81/1A	Ammonite	+ 18.0
OCS 81/1B	Ammonite	+ 7.8
OCS 81/2A	Nucula	- 6.7
OCS 81/2B	Nucula	- 1.0
OCS 81/2C	Nucula	+ 6.1
OCS 81/9A	Ammonite	+ 8.1
OCS 81/9B	Ammonite	+ 11.6
OCS 81/17		
S17/1	Nucula	+ 13.5
S17/2	Ammonite	+ 16.8
S17/3	Ammonite	+ 15.4
S17/4	Grammatodon	- 8.3
OCS 81/16		
S16/1	Nucula	+ 5.2

Ammonite Concretions

Sample	Sample Description	δ34S CDT
OCC81/L2 A	Pyrite Replaced Ammonite Shell	+ 29.5
B	Pyrite Replaced Nucula Shell	+ 17.8
C)	Surrounding Edge	+ 10.4
D)	Concretionary Middle (	+ 28.6
E)	Pyrite (	+ 36.8
F)	Edge	+ 16.2
OCC81/L1 B	Concretionary Pyrite	+40.0
C	Pyritized sediment trapped in the concretion	+ 24



Fig 1. Map of Lower Oxford Clay Localities in England.  
S=Stewartby, B=Bletchley, C= Calvert and NC=  
Norman Cross Peterborough

FIGURE 1

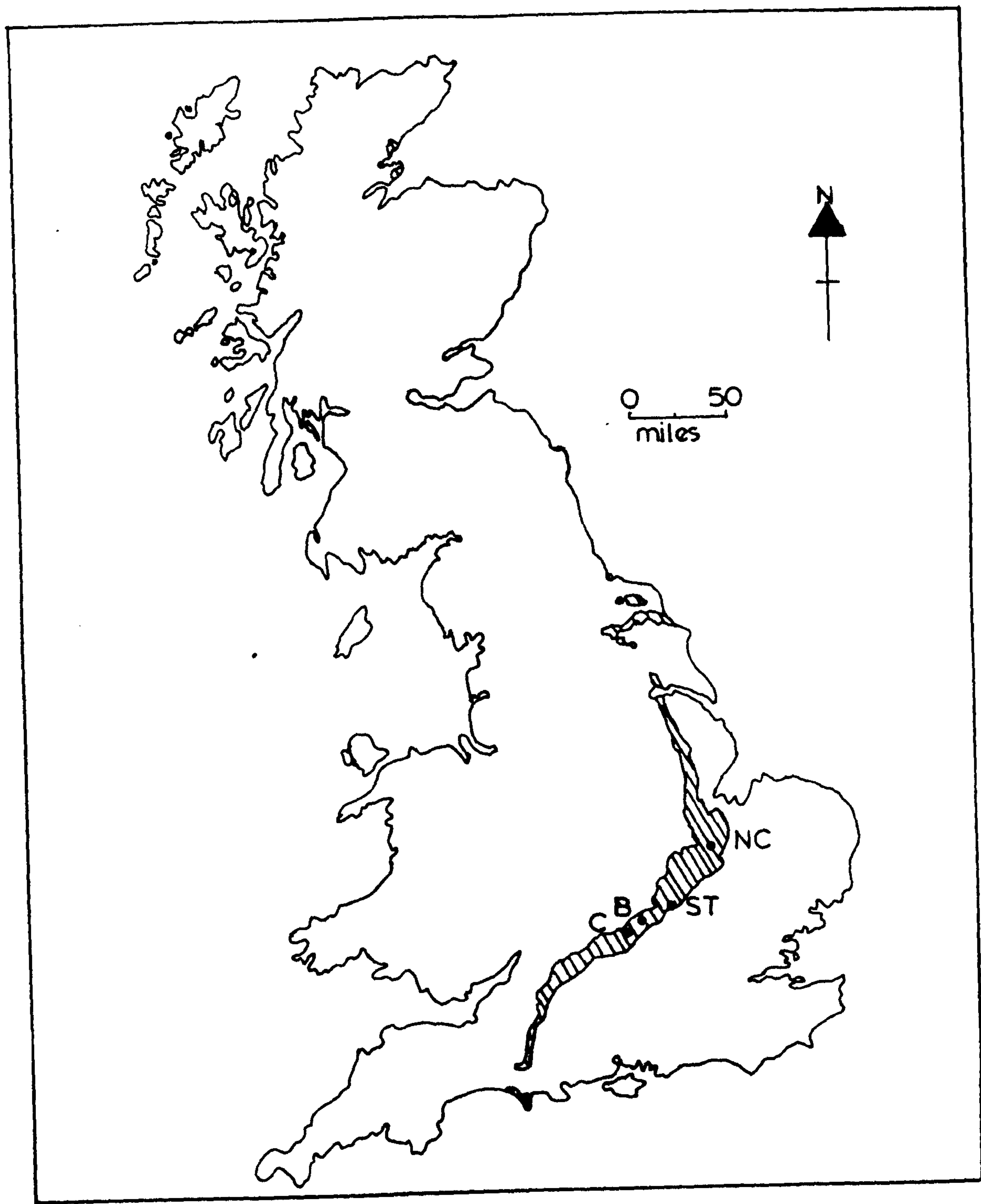


Fig 2. Biofacies distribution in Lower Oxford Clay pits after Duff (1975). Numbers indicate sampling points. Sample prefixes are Stewartby OCS81/, Norman Cross OCN81/, Calvert OCC81/, Bletchley, OCB81/.

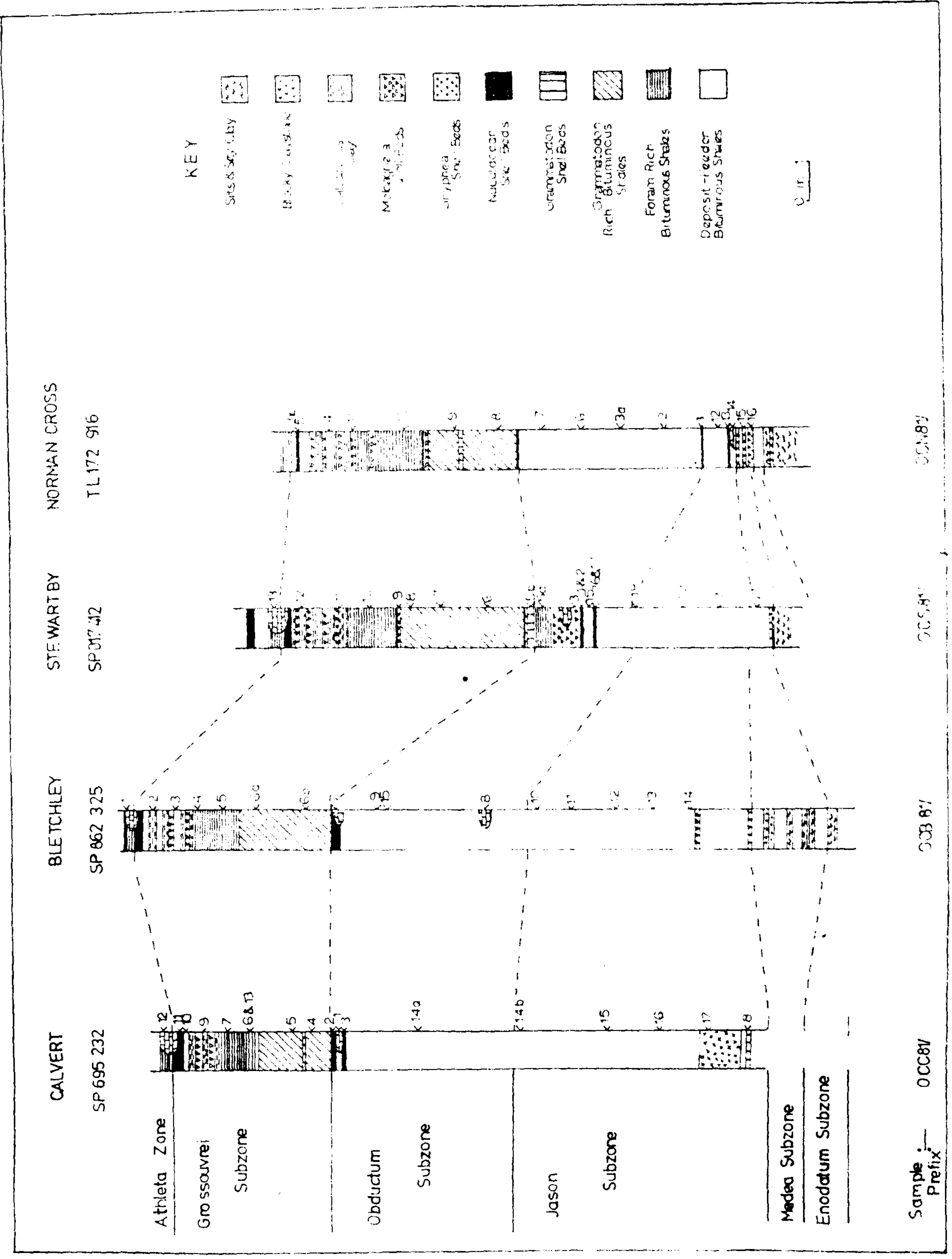
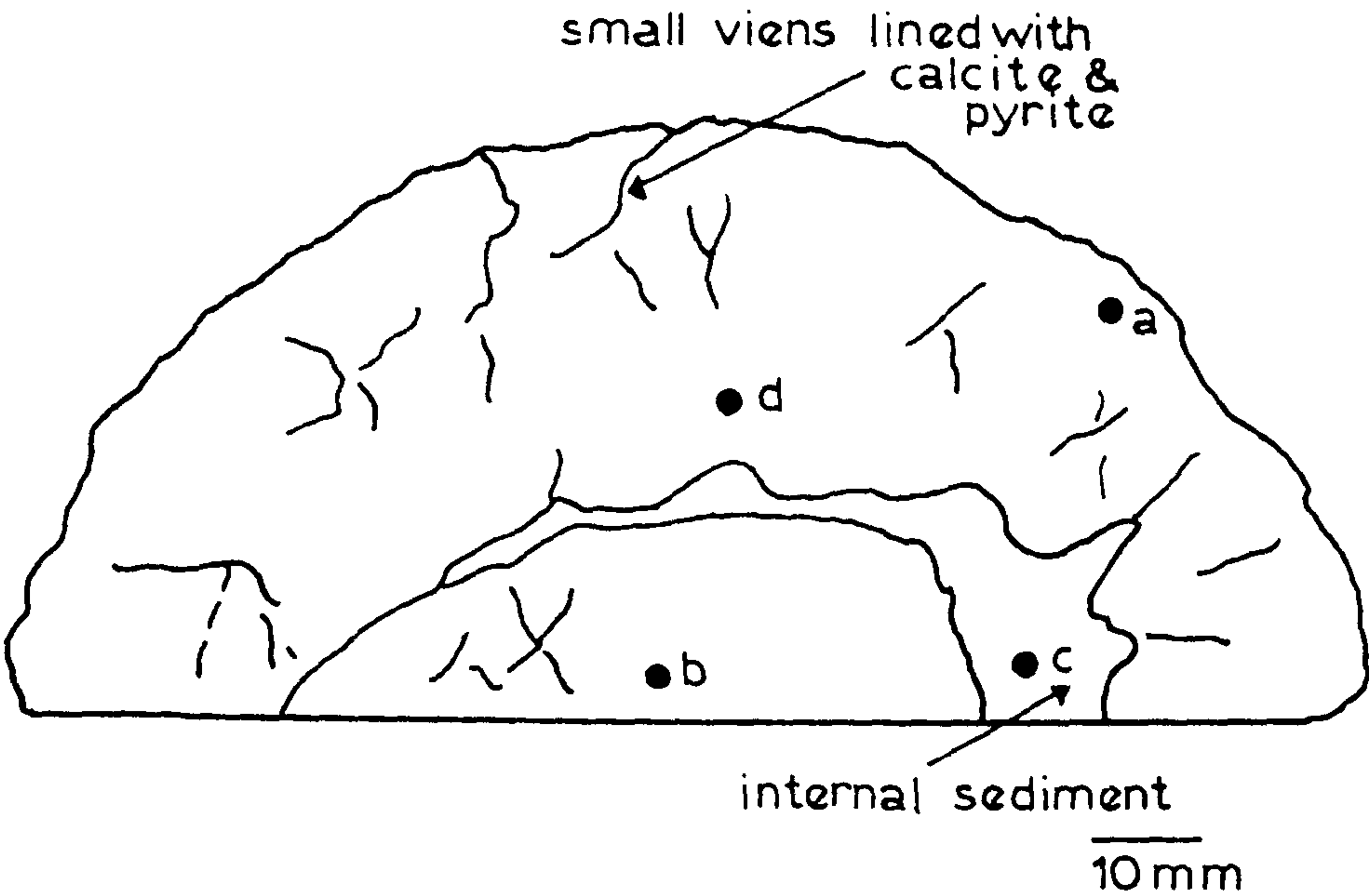
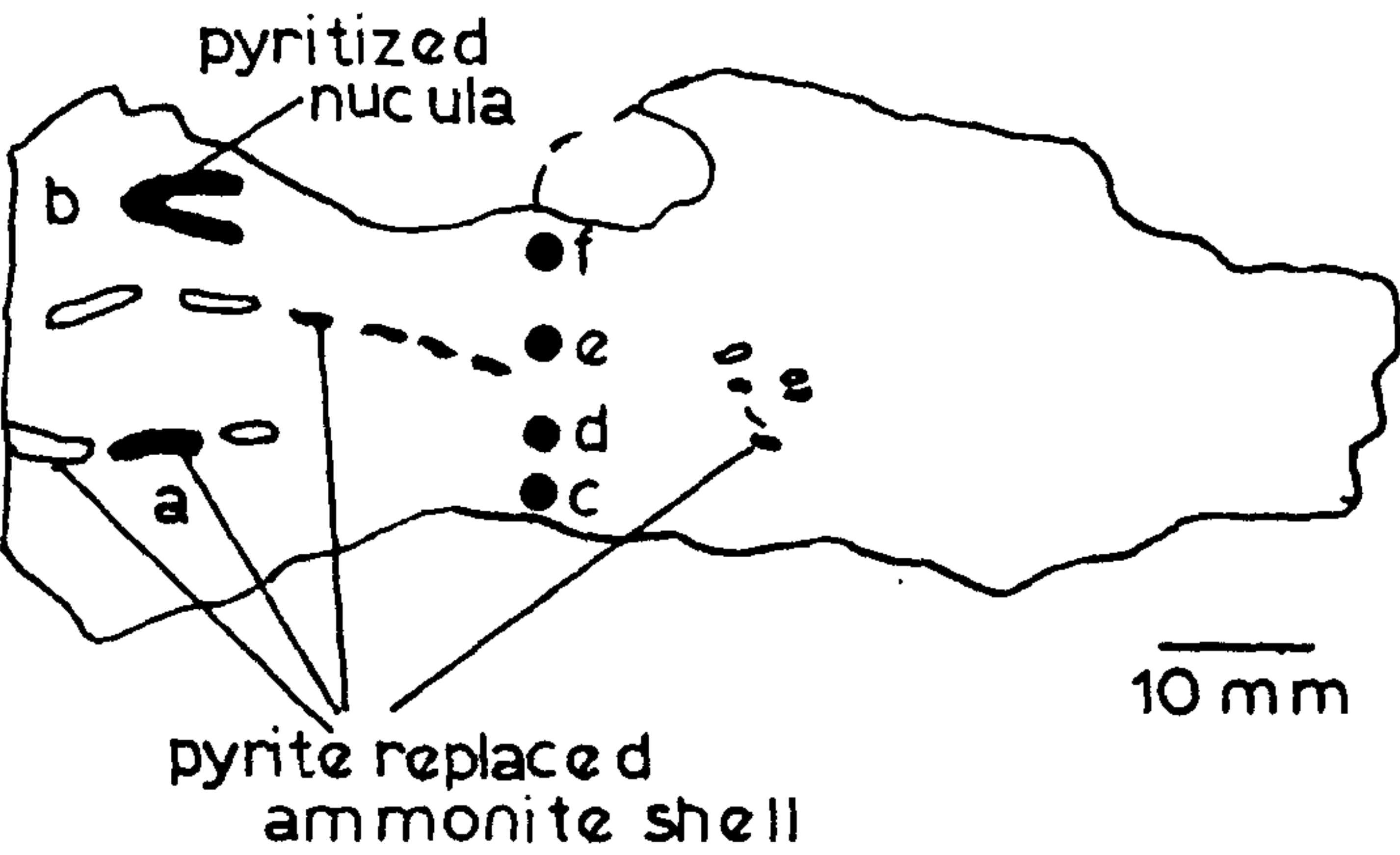


FIGURE 3



OCC 81/L1



OCC 81/L1

SAMPLES FROM AMMONITE CONCRETIONS

Fig 4 & 5 Histograms of data from Lower Oxford Clay.

Deposit feeder shales plain squares; Foram-rich shale f; Grammatodon shales g. Calcareous clays c; Blocky claystone b. Capital letters indicate means of data for each biofaces, D indicate deposit feeder shales. 4A Carbonate carbon G=0.97,  $\sigma$ =0.60; D=1.00,  $\sigma$ =0.66; F=1.38,  $\sigma$ =0.85; C=3.01,  $\sigma$ =1.13. 4B Organic carbon C=4.44,  $\sigma$ =1.08; G=4.58,  $\sigma$ =1.59; D=4.79,  $\sigma$ =1.68; F=7.19,  $\sigma$ =1.65. 5A Pyrite sulphur D=1.45,  $\sigma$ =0.22; C=1.15,  $\sigma$ =0.29; G=1.125,  $\sigma$ =0.27; F=1.057,  $\sigma$ =0.22.

Fig 5B gives all the isotope data for the Lower Oxford Clay. V indicate means of various groups for data, see text.



FIGURE 4

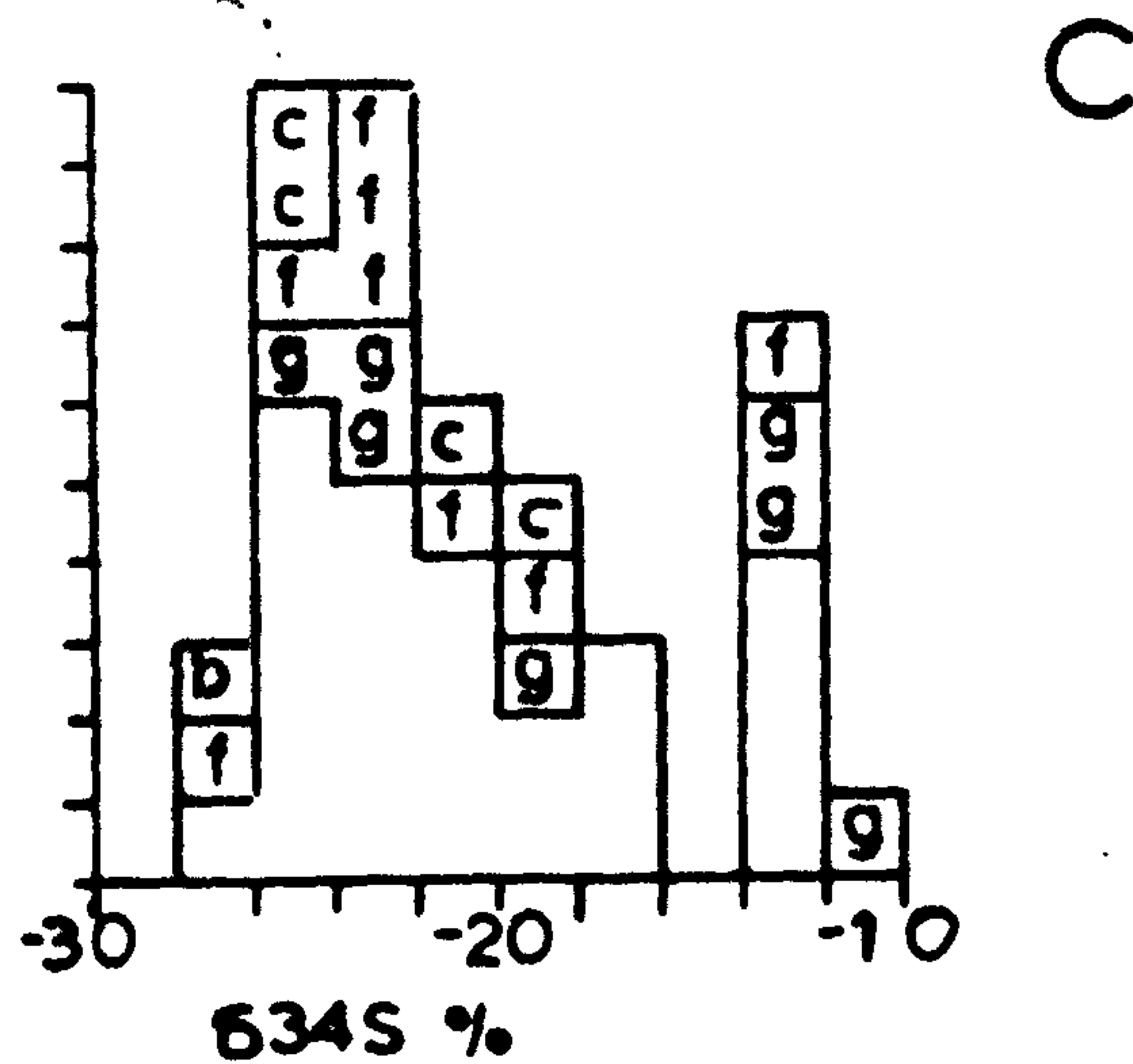
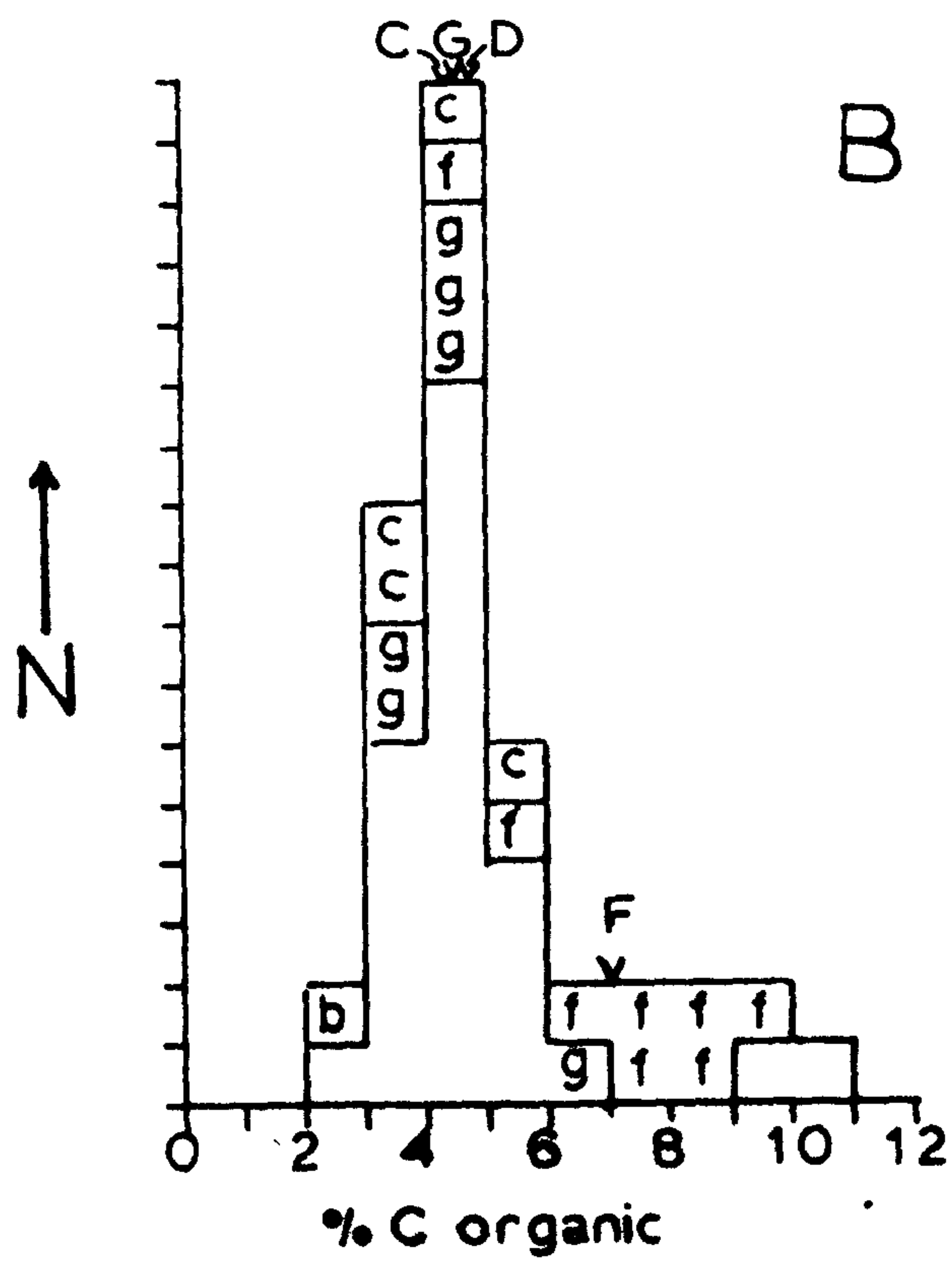
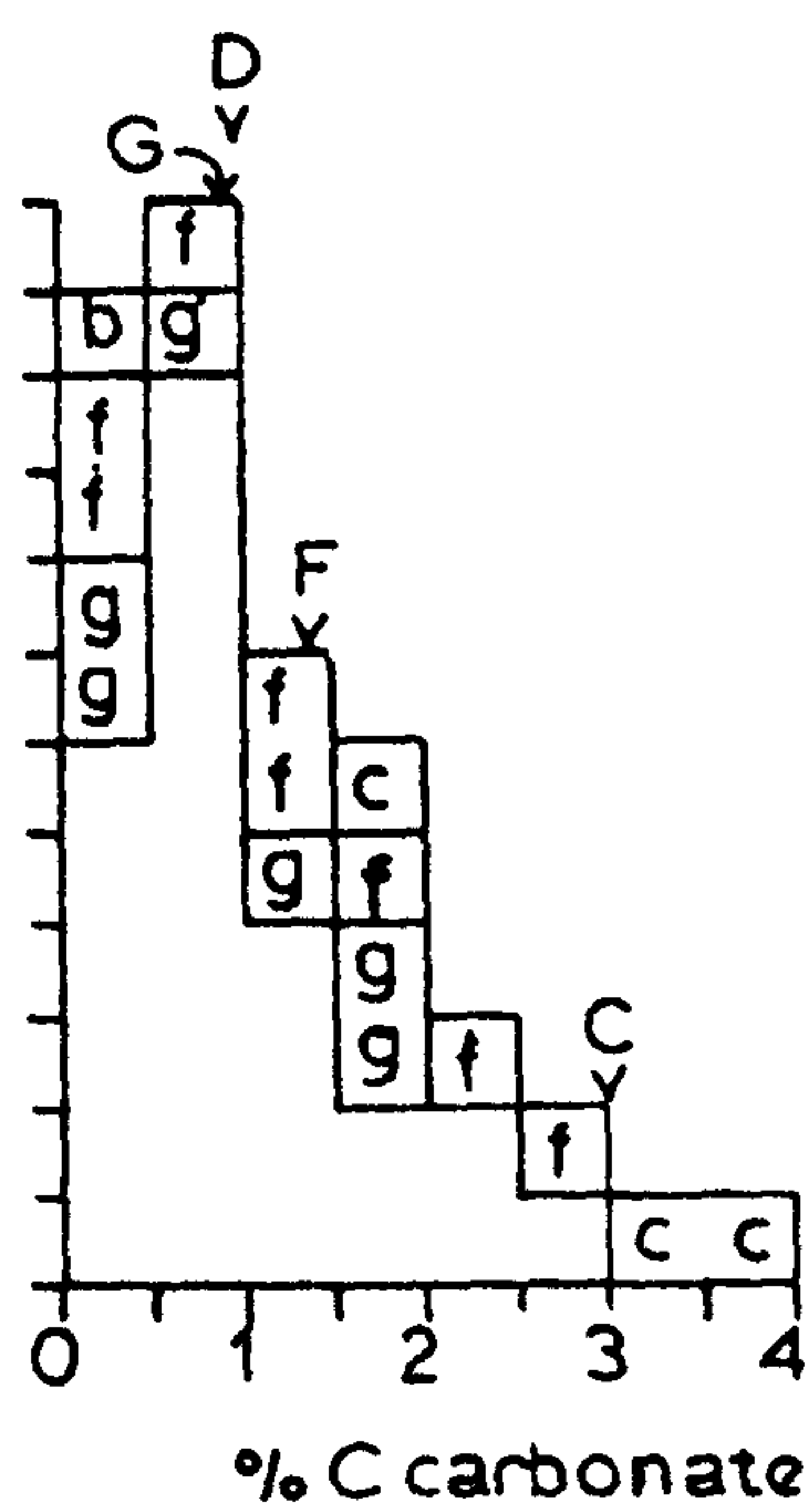


FIGURE 5

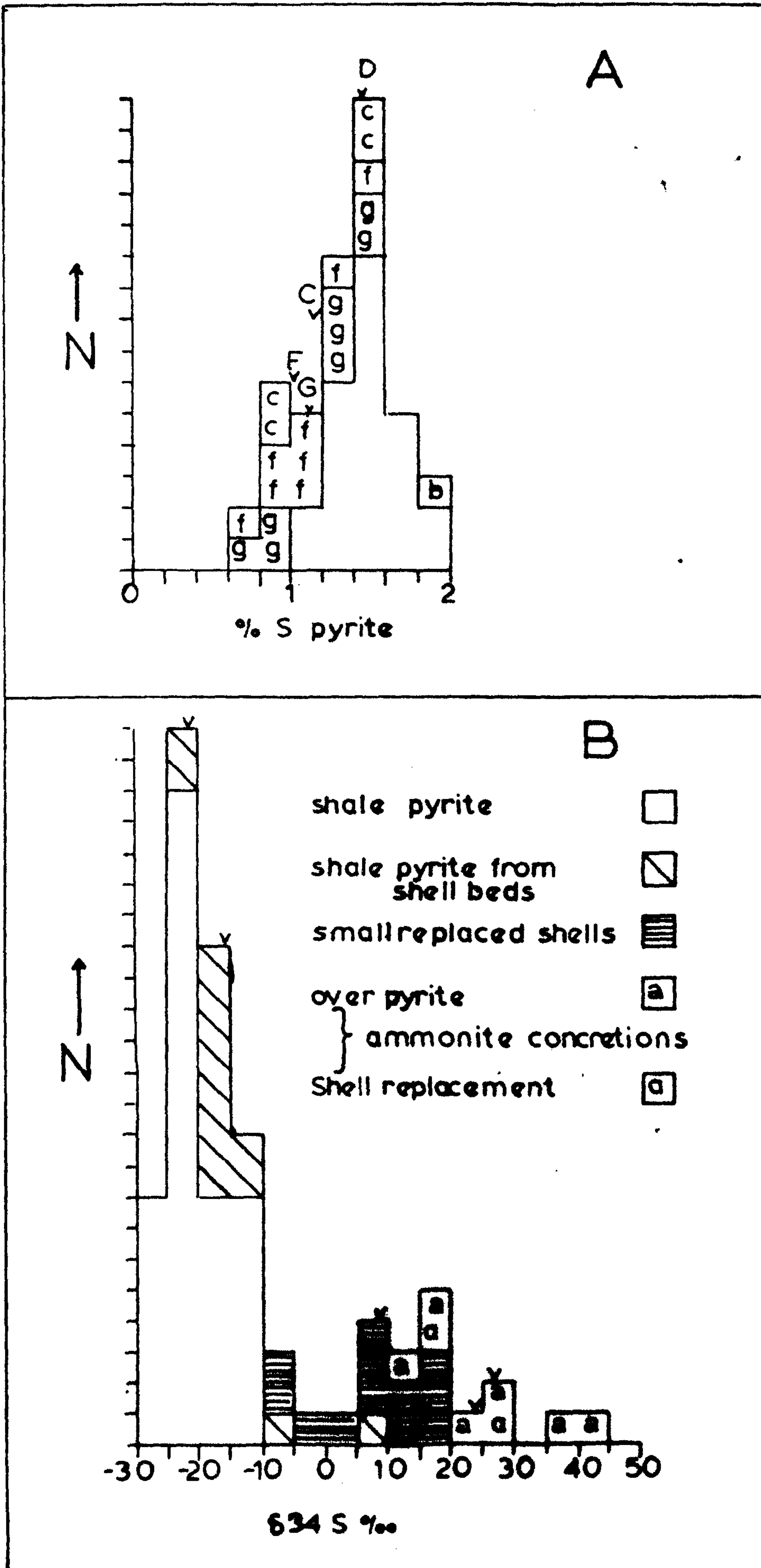
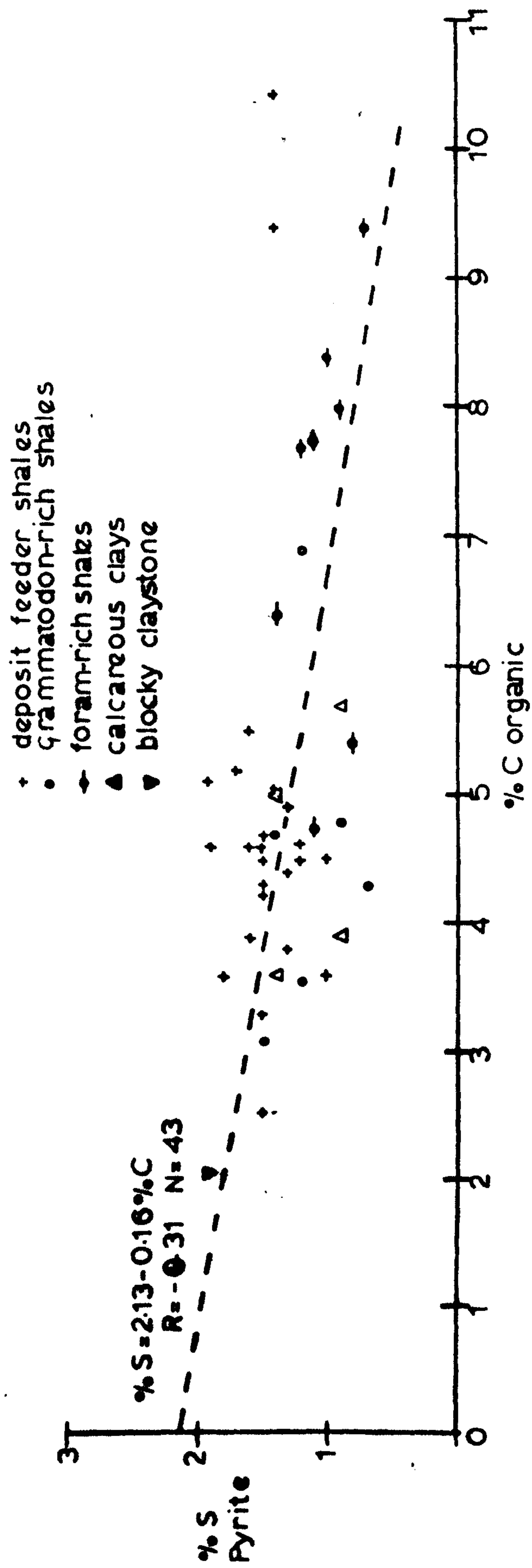


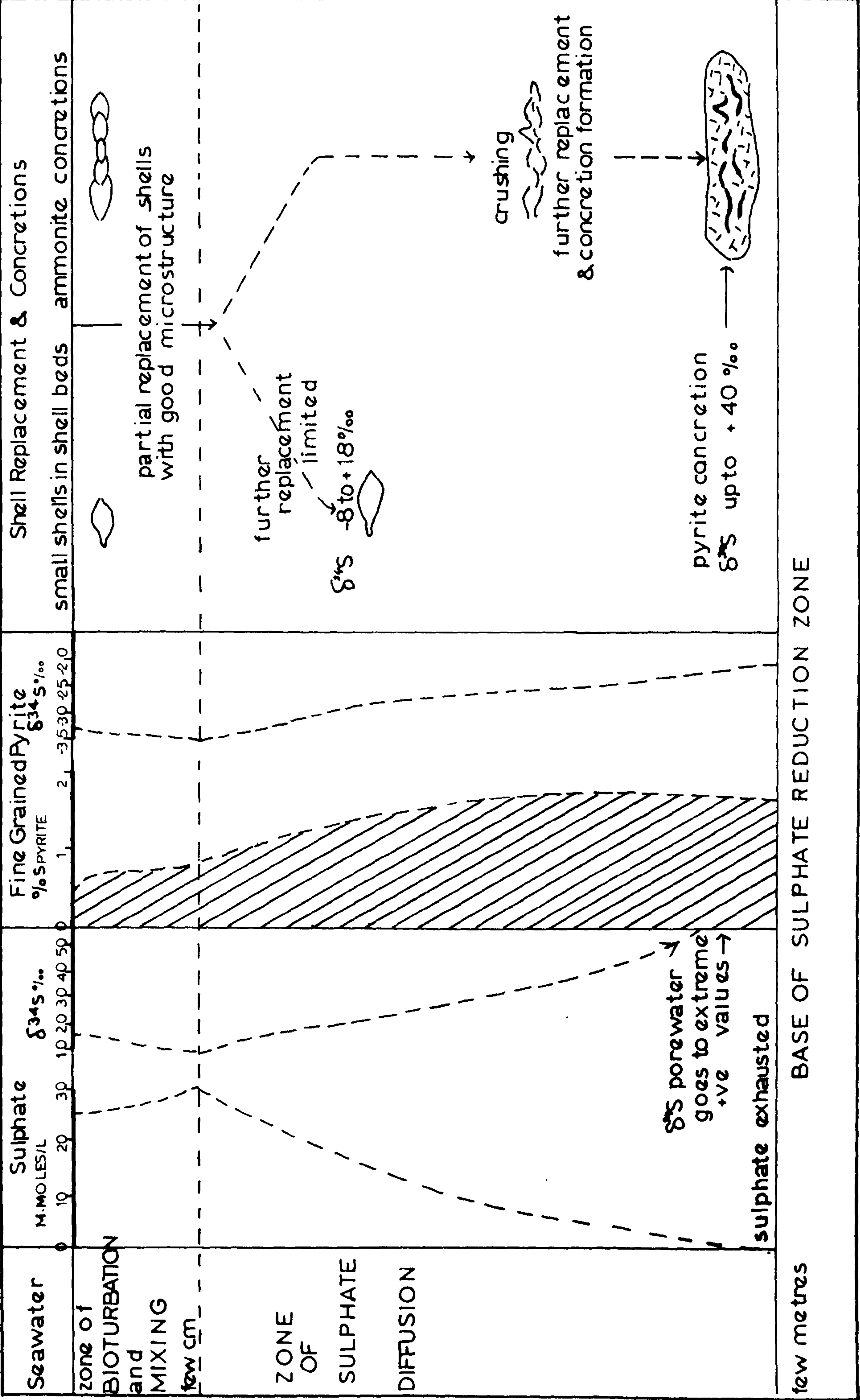
Fig 6. Plot of Pyrite sulphur content Vs Organic Carbon Content.



**Fig 7.** Summary of supposed variations of sulphur content and  $\delta^{34}\text{S}$  values for porewater sulphate and fine-grained pyrite with depth, and the stages of replacement of shells and associated concretionary pyrite formation.



FIGURE 7



# Pyrite Formation and the Environment of Deposition of Laminated Jurassic Bituminous Shales from South Germany and Scotland.

### 1. Introduction

The formation of pyrite in sediments is controlled by the presence of anaerobic conditions and the supplies of organic carbon, sulphate and iron. Variations in the environment of deposition may alter the relationships between these factors and hence the amount and isotopic composition of pyrite formed. In the present research programme various Jurassic shales and clays have been studied to determine the factors which affect the amount and isotopic composition of pyrite and their variation between and within different shale and clay environments.

In this chapter two Jurassic examples of the "Bituminous shale" facies of Morris (1979, 1980) are described; the Posidonia Shales of southern Germany and the Dunans Shale (Callovian) of Skye. The Posidonia Shales are the contemporaneous equivalent of Morris' type Jet Rock. This shale facies is characterized by good lamination undisturbed by bioturbation and by a bivalve fauna which consists mainly of epifaunal suspension feeders with infaunal types rare or absent.

The Posidonia Shales has been extensively studied in recent years mainly as a result of the exceptional

preservation of vertebrate and other fossil material it contains. It has been subject to various interpretations of which two are of particular interest.

1. The widely accepted belief is that the Posidonia Shales represent an anaerobic epicontinental marine basin (Seilacher & Wesphal 1971). Seilacher (1970) described it as a "Type A" Fossil-Lagerstätten; a sediment yielding an unusual amount of palaeontological information due to exceptional preservation resulting from oxygen depletion in the water column restricting predation, scavenging, deposit feeding, and aerobic bacterial decay. Occasional layers occur in which the anaerobic conditions appear to have ameliorated and the seafloor has become temporarily colonized.

2. Kauffman (1978) postulated that a sharp  $O_2/H_2S$  boundary fluctuated between the the sediment/water interface and the overlying water column as a result of algal mat formation.

Küspert (1982) published the results of a stable isotope and organic geochemical study, in which he divided Posidonia shales into three facies A, B and C. He proposed that low  $\delta^{13}C$  values of carbonate and organic carbon in facies A resulted from the mixing of dissolved light, sulphate-reduction-derived carbon with the overlying water lowering the C isotope content of the Dissolved Inorganic Carbon (D.I.C.) pool and so resulting in the lightening of both carbon and carbonate

formed from this pool. Küsspert suggested that such circumstances could not result from the algal mat model of Kauffman and required extensive stagnation of the water column. In facies B & C aeration improved and allowed occasional sea floor colonizations.

There are therefore two possible models, one suggesting a highly stagnant environment with extensive stagnation of the water column, the other suggesting limited stagnation of the water column and large periods of time where the sediment surface was habitable. Theoretically these two models would be expected to produce different S isotope and pyrite content patterns, which might presents a means of testing the two models.

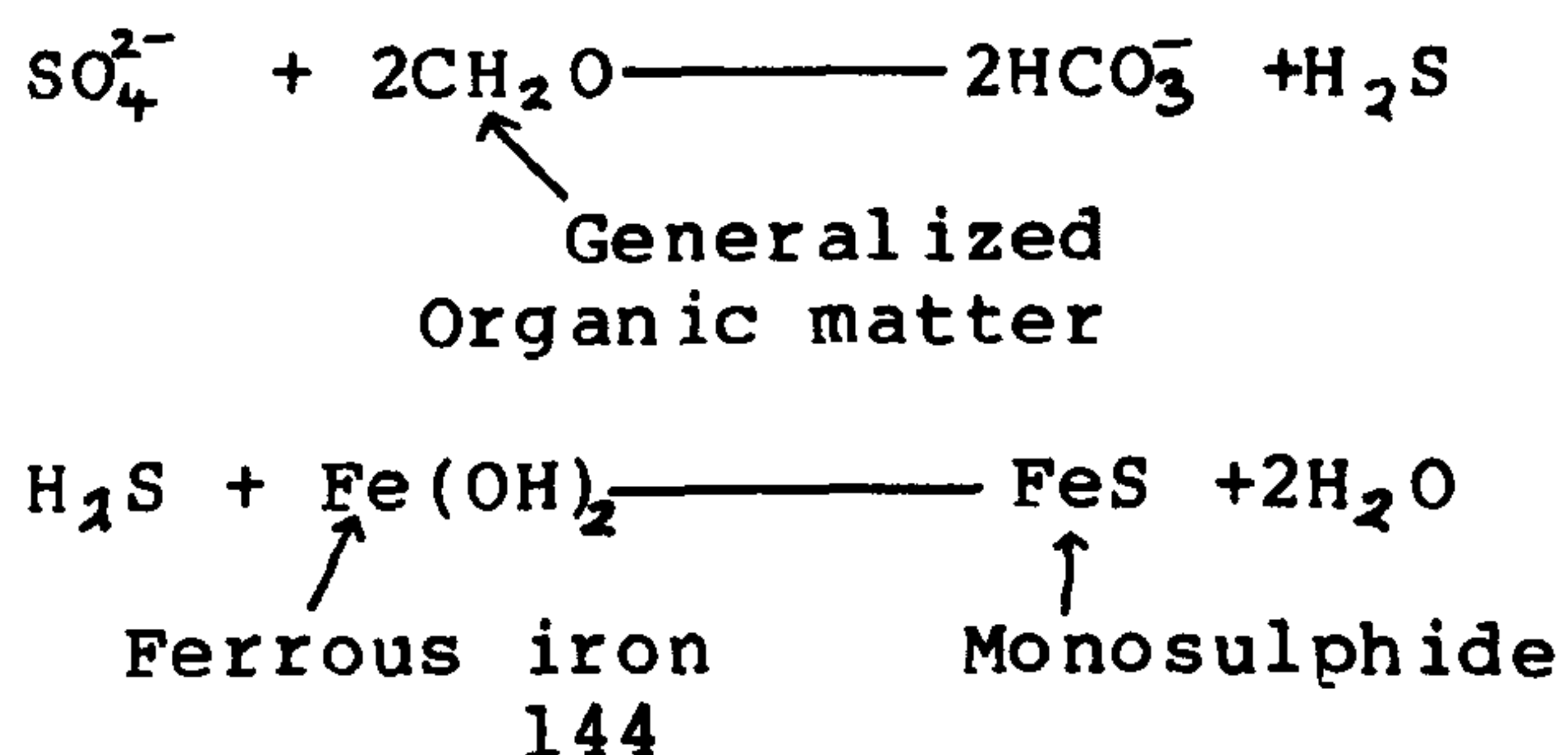
The Dunans Shale has been less extensively studied. It constitutes the lowest member of the Staffin Shale Formation (Turner 1966), and consists of just over 7m of laminated shales. At the base are thin intercalations of glauconitic silts and about 3m above the base is a prominent band of laminated bituminous shales which become less bituminous upward with a further glauconitic bed near the top (Sykes 1975). The glauconitic sands yield abundant Cylindroteuthis and some paler beds a bivalve fauna. The laminated bituminous shales contain only belemnites and Lingula at one horizon. Ammonites at the base of the section indicate a Callovian (jason zone) age, but above 1.2m ammonites are not found (Sykes 1975, Sykes and Callomon 1979). The lack of macrofauna



is also reflected in the microfauna with no foraminifera (Sykes 1975) and ostracoda (Whatley 1970). The top of the section is believed to be of athleta age (Sykes 1975, Sykes & Callomon 1979) although it is not directly datable. The sequence probably represents a transgressive episode leading to a peak in the highly bituminous horizon 3m up followed by a regressive episode; this sequence corresponds to that seen in the Lower Oxford Clay of England (Duff 1975). The barren nature of the sediment implies a high degree of anoxia in the overlying water with the occasional more oxic interval where Lingula, which is tolerant of low oxygen conditions, occurs.

## 2. Causes of Variation in Pyrite Sulphur Content.

The formation of pyrite in marine sediments is due to the action of sulphate-reducing bacteria on the seawater sulphate to form sulphide, which reacts with iron to form pyrite either directly or via a monosulphide precursor (Goldhaber & Kaplan 1974). The reactions may be summarized as follows:





The iron monosulphide (mackinawite) may proceed to pyrite by the addition of elemental sulphur. If the reaction proceeds via a greigite phase ( $\text{Fe}_3\text{S}_4$ ), then the characteristic framboidal texture results (Sweeney & Kaplan 1973). The formation of greigite from mackinawite is an oxidation reaction, suggesting that the formation of framboids requires conditions which are not totally anoxic. Hudson (1982) notes that, though present, the framboids in the Posidonia Shales were smaller than those found in the more oxic environments.

There are three prerequisites for sulphate reduction to occur; 1. anoxic conditions, 2. sulphate 3. organic carbon. The formation of pyrite also requires iron.

1. Anoxic conditions in which the sulphate-reducing bacteria may function, as they are obligate anaerobes. As indicated above it is supposed that for at least some of the time the overlying water column in the Posidonia Shales and the Dunans Shale were anoxic, and it is supposed that below the sediment/water interface they were permanently anoxic. It is not necessary for the overlying water to be anoxic for the formation of pyrite to occur: the anoxic condition will be served equally well by reducing microenvironments in an otherwise oxidising sediment or by anoxic sediment underlying a thickness of oxidising.

2. Sulphate, the chief source of which in marine

environments is seawater. If reduction occurs within the water column then the sulphate-reducing bacteria are in contact with an essentially infinite reservoir. Sulphate is supplied to the sediment, over and above that buried with it, by diffusion, the gradient being controlled by the rates of bacterial reduction (Berner 1980).

3. Organic matter is necessary as the material on which the bacteria feed. A general covariance between organic carbon and pyrite sulphur has been noted by several authors (Berner 1970, Sweeney 1972, Sweeney and Kaplan 1974). Higher initial concentrations of organic matter result in the formation of greater quantities of sulphide. If the proportion of organic matter utilized in sulphate reduction is constant then a positive correlation between organic C and pyrite S will result. Sweeney (1972) demonstrated for a range of recent sediments an average C/S ratio of 3. In euxinic conditions C/S ratios consistently less than 3 and regression lines with positive intercepts on the S axis have been demonstrated (Leventhal 1983, Berner & Raiswell 1983). These result from larger proportions of metabolisable organic matter entering the sulphate reduction zone, as its exposure to aerobic degradation has been limited (Zolnay 1971), and from a decoupling of the organic matter from its complementary sulphide (Leventhal 1983).

4. Iron is necessary for the conversion of bacterially

produced H<sub>2</sub>S to iron sulphide. Iron is supplied to the sediment in detrital minerals and as iron oxide coating on grains and is in the ferric form. H<sub>2</sub>S may react in situ with ferric iron and simultaneously reduce and precipitate it as iron sulphide (Berner 1969, Sweeney 1972). When all in situ iron is consumed then the H<sub>2</sub>S will be free to diffuse away from the site of reduction, unless iron is also free to diffuse, this only being so when it is in the ferrous form. If the conditions are totally reducing then iron will be in the ferrous form and free to diffuse. If the conditions are not totally reducing then H<sub>2</sub>S may be lost into oxidising environments (Chapter 2). If sufficient organic carbon and sulphate is present to maintain a high H<sub>2</sub>S concentration then the total amount of pyrite formed will be limited by the the amount of iron present. This will result in a modification of the C/S ratio from that which would be expected as not all the the sulphide formed will be represented as pyrite. The incomplete trapping of H<sub>2</sub>S will result in it being able to diffuse through the sediment and into the overlying water.

### 3. Controls of $\delta^{34}\text{S}$ Fractionation

Three factors may affect the  $\delta^{34}\text{S}$  value of fine-grained pyrite formed in shales and clays:

1. Natural fractionation, the fractionation between

sulphate and the sulphide produced from it.

2. The  $\delta^{34}\text{S}$  value of sulphate . The chief source of sulphate is seawater which in the Jurassic had an sulphur isotopic composition of +16‰ (Claypool et al 1980). If the environment of sulphate reduction becomes closed or partially closed to the access of sulphate this value will change becoming enriched in  $^{34}\text{S}$  due to the formation of isotopically light sulphide.

3. The proportion of sulphide formed at each stage of burial, either within a closed or open system.

Fractionation factors for bacterial sulphate reduction have been experimentally investigated by several authors (a good review is given by Chambers and Trudinger 1979). Experiments have shown isotopic effects between +3 and -46‰ and indicate that the greatest fractionations are obtained at the slowest specific rates of reduction. The smallest fractionation +3‰ was obtained at low concentrations of sulphate (0.01mM) (Harrison and Thode 1958). It has been suggested that, at extremely low rates of reduction, fractionations may approach those of equilibrium , -74‰ at 25°C (Tudge and Thode 1958, Trudinger and Chambers 1973).

A compilation of fractionation factors given by Chambers and Trudinger (1979) show that fractionations in recent sediments range between -34 and -59‰ with a mean of about -50‰ and for reduction occurring in



anoxic water columns a mean of  $-43\text{‰}$ . These values are much lower than those generally found in experimental cultures. Rees (1973) suggested that fractionations of  $-50\text{‰}$  in the Black Sea were the effect of the operating conditions of the sulphate-reducing bacteria, where slow specific rates of reduction allow the recycling of sulphur within the metabolic pathway. He speculates that this is brought about by a bacterial population which has grown to a point where it utilizes all organic matter as it is supplied.

If sulphate reduction takes place in a totally open system, eg. anoxic water column, the sulphate reservoir can be considered to be essentially infinite and the removal of isotopically light sulphide does not affect the  $\delta^{34}\text{S}$  of the reservoir sulphate. Within the sediment the system may become closed or partially closed to the access of seawater, and sulphate is supplied to the system by diffusion (Goldhaber and Kaplan 1980); in this case the preferential removal of  $^{32}\text{S}$  by the bacteria enriches the remaining sulphate in  $^{34}\text{S}$ ; in a process similar to Rayleigh distillation. If the reduction goes to completion the resulting sulphide would be expected to have the isotopic composition of the initial sulphate, that is seawater values. Goldhaber & Kaplan (1980) demonstrated that the preferential removal of  $^{32}\text{S}$  acts to enhance the diffusion of that isotope and the resulting sulphide is consequently



lighter than the supposed seawater value, somewhere in the region of seawater-25‰ assuming a fractionation factor of -45‰.

We may therefore consider that there are two zones in which sulphate reduction may occur:

1. An open system zone in an anoxic water column or bioturbated sediment.
2. A partially closed system zone in which sulphate is supplied by diffusion

The former results in sulphide with an isotopic composition of about seawater-50‰ and the later seawater-25‰. The resulting isotopic composition of the fine-grained pyrite will be the sum in proportion of the pyrite formed in each zone. Using this model Goldhaber and Kaplan (1980) were able to model the isotopic composition of sediments from the Gulf of California. When a large portion of the water column is anoxic then the majority of the pyrite is formed at or above the sediment/water interface with an isotopic composition biased towards the light open system values (Schwartz and Burnie 1973).

#### 4. Sample Collection and Preparation.

Samples of the Dunans shale were collected from the exposures at Staffin Bay (NG 472 708 point 5 as defined by the in the Skye Memoir, Anderson and Dunham, 1964). Section and sampling points are given in figs 1. The

Posidonia Shale material was supplied as powders, by Wölfgang Küsspert from the core material of the bore holes at Zimmern near Hechingen and Nürtingen Württemberg southwest Germany. The sections and sampling points are shown in fig 2. The values for  $\delta C$  organic  $\delta C$  carbonate and the carbon isotope data are those of Küsspert, for details see Küsspert 1977, 1981 & 1982.

The samples of the Dunans Shale were prepared as powders by Tema milling. They were analysed for organic and carbonate carbon by a two stage wet chemical technique a modification of Bush (1970), in which the sample is first reacted with analar phosphoric acid to liberate  $CO_2$  from the carbonate which is then trapped in a known volume of standard  $Ba(OH)$  solution. The  $Ba(OH)$  is then back titrated against standard  $HCl$  solution. Saturated chromic acid is then added to the sample solution to liberate the organic carbon as  $CO_2$  which is then treated in the same manner as the carbonate  $CO_2$ .

Sulphur for isotopic analysis is extracted from the powders of both the Dunans and Posidonia Shales using a quantitative high temperature oxidation with cuprous oxide (Robinson and Kusakabe 1975) using an extraction line set up as described by Coleman and Moore (1978). It was found necessary to pre-treat samples to remove carbonate and organic carbon, which during extraction liberate  $CO_2$  which interferes with the extraction. The samples were first treated with 10% acetic acid followed

by 12hrs reaction in an oxygen plasma using a Nanotech Plasmaprep P100, which serves to oxidise at low temperature ( $150^{\circ}\text{C}$ ) any organic matter, so as well as removing any organic carbon it should also remove any organically bound sulphur. Both treatments were undertaken quantitatively so that the  $\text{SO}_2$  yield would be a measure of the pyrite sulphur content. The  $\text{SO}_2$  was analysed on a V.G micromass 602c mass spectrometer with heated inlet. The raw data were corrected for isobaric and instrumental effects (Coleman 1980).

HCl extractable iron was determined using a method similar to that of Berner (1970), 0.2g of sample was boiled with 3ml of concentrated HCl for 2min in a hot block. The liquid was then diluted to 10ml and analysed on a Perkin Elmer Atomic Absorption Spectrometer.

Results are presented in tables 1 and 2 analytical precision was as follows. Pyrite sulphur content although variable depending on sample size and quantity of  $\text{SO}_2$  evolved is generally better than 0.1%. The analytical uncertainty in any sulphur isotopic determination is 0.05% the reproducibility between two laboratory standards extracted and analysed is normally better than 0.2%. In the case of shale samples the reproducibility was somewhat worse but no more than 0.7%. Organic carbon and carbonate (Dunans Shale) are better than 0.1% and HCl extractable iron better than 0.1%.

5. Results The results are presented in tables 1 and 2.

#### 5.1 Pyrite Sulphur and $\delta^{34}\text{S}$ Variations (Fig 3)

The pyrite sulphur contents show a broad range of values between 1.6 and 4.9%S. The Dunans Shale shows a significantly higher mean %S (3.1 compared to 2.4%) and has a wider spread of compositions (6=1 compared to 0.46). Within the Posidonia Shales there is some variation between the facies, although it is not statistically significant. The samples from facies A tend to have higher %S values than B and C: apart from sample 224 (table 1), which coming from a limestone horizon shows dilution by diagenetic carbonate.

The Dunans Shale has a lower mean  $\delta^{34}\text{S}$  (-32.7‰) compared to the Posidonia shales (-23.6‰), With Jurassic seawater at +16‰ (Claypool et al 1980) these represent isotopic displacements ( $\Delta^{34}\text{S}$ ) of -48.7‰ and -39.6‰. The most negative values come from the Dunans Shale and represent  $\Delta^{34}\text{S}$  of -57‰. The heavier values from the Posidonia shales (-16.6‰) suggest a significant influence of closed system reduction and not the dominantly -50‰ fractionations suggested for euxinic environments.

#### 5.2 Organic Carbon (Fig 3)

The Posidonia Shales and the Dunans Shale show distinct differences in their organic carbon compositions. The

Dunans Shale has a mean of 5.71% and the Posidonia Shales 8.85%. The variation of organic carbon in the Posidonia Shales is ascribed by Küspert (1982) to dilution by later carbonate. Although this accounts for much of the variation some of the extreme values must represent changes in the organic supply. The lowest %C organic (2.4%) in the Posidonia Shales is in the sample from the Middle Ashgrey Shales. The distinction between the Posidonia Shales and the Dunans Shale is further accentuated when the carbonate carbon is taken into account; the Dunans Shale having a minimal carbonate content (< 1% carbonate carbon) compared to the considerable amounts of in the Posidonia Shales.

Fig (4) shows a plot of %S pyrite Vs %C organic for the Posidonia Shales and the Dunans Shale; best fit lines have been plotted though neither has a significant correlation coefficient. The majority of Posidonia Shales points plot not to the left hand side of the Sweeney Line , as would be the case for euxinic conditions ( Leventhal 1983). The Dunans Shale Samples lie on the left of the Sweeney Line as would be expected.

### 5.3 Iron:

The results of available iron determinations are presented in two ways, 1. as %FeHCl and 2. in terms of the Degree of Pyritization.(D.O.P.)



$$\text{D.O.P.} = \frac{\% \text{Fe as Pyrite}}{\% \text{Fe as Pyrite} + \% \text{FeHCl}} \quad (1)$$

The results of the Posidonia Shales and the Dunans Shales are quite distinct. The Posidonia Shales has low %FeHCl (<0.5) and the D.O.P. large (>0.8). The Dunans Shale has an extremely broad range of values for %FeHCl (0.59 to 3.16) and a correspondingly wide range of D.O.P.

The values of %FeHCl is a measure of the iron still available for pyrite formation. Berner (1970) demonstrated that the solution of iron minerals in hot concentrated HCl is similar to their reactivity with H<sub>2</sub>S. The high concentration of HCl used in the preparation, probably leads to the solubilization of greater quantities of iron than would react with the relatively low concentrations of H S in sediments. It would therefore be expected that the %FeHCl is an overestimate of the iron available for pyritization and the D.O.P. an underestimate. The D.O.P. has a theoretical value between 0 and 1, the latter occurring when the available iron is exhausted. From the above considerations it is unlikely that the value will actually reach 1 even when iron is limiting. The values of D.O.P. and %FeHCl are susceptible to the effects of weathering, which produces iron oxides and so yields spuriously high values of %FeHCl and low values of D.O.P. the Posidonia Shale material is from boreholes

and should not suffer from this problem. The Dunans Shale does appear to show the effects of such weathering, having a rusty outward appearance at some levels. Although it was attempted to sample non-weathered portions of the rock, this was probably not achieved. This may account for the extremely high %FeHCl value of 3.16%, and the large range of values. the relatively low %FeHCl and high D.O.P.s suggest that iron was limiting pyrite formation in the Posidonia Shale. The D.O.P. values for the Dunans Shale are inconclusive but might suggest some limitation of iron if they are assumed to be minimum values due to the effects of weathering.

### 6. Discussion

From the high D.O.P. values it would appear that iron is the limiting factor for pyrite formation in the Posidonia Shales. The Dunans Shale data is more ambiguous and although it is suspected that Fe is the limiting factor here also, limitation by organic carbon cannot be totally ruled out.

The relatively high  $\delta^{34}\text{S}$  values for the Posidonia Shales would suggest that a significant proportion of the sulphide was formed in a closed system within the sediment. This might suggest that the extent of reduction in the overlying water was limited. This does

not compare with the models that suggest extensive stagnation, where most of the reduction takes place in the water column and little in the sediment.

Lack of Fe may limit the formation of pyrite but it does not limit sulphate reduction; that lies in either sulphate or organic carbon. The continuation of sulphate reduction beneath the depth where Fe has been exhausted will generate free  $H_2S$  which will be free to diffuse away from the site of reduction and into the overlying sediment and water column. On diffusing upwards through the sediment this  $H_2S$  may precipitate and contribute to the isotopic composition as pyrite. As a result the pyrite formed may be isotopically heavier than would be expected if this diffusion were not taken into account.

The isotopic data and C/S ratios for the Dunans Shale is more in keeping with a model implying more extensive stagnation of the water column, with a mean  $\Delta^{34}s$  of -48.7‰, being dominated by the open system water column reduction and C/S ratios <3. The higher Dunans Shale pyrite sulphur contents would suggest that, if conditions were similar to the Posidonia Shales, more of the heavy, closed system H S might have been trapped, but the light isotopic values do not indicate this. It seems therefore that sulphate reduction did not continue deep into the zone of diffusion and that reduction of sulphate was incomplete. This might suggest that sulphate reduction, as opposed to pyrite formation,

was limited by organic carbon. It is also noticeable that the most negative values in the Posidonia Shales (-32.4 ‰ -33‰) are from the samples with the lowest organic carbon contents suggesting that in these cases organic carbon may have been the limiting factor in sulphate reduction.

It therefore appears that although the Posidonia Shales and Dunans Shale are ostensibly the same facies there are distinct differences between the two. The differences may lie in the depositional character of the two shales, particularly the organic carbon concentration and the extent of anoxic water. If sulphate reduction is limited by organic carbon, as suggested for the Dunans Shale, then reduction of sulphate will not go to completion and the heavy sulphide will not be formed. If sulphate is limiting reduction does go to completion and the heavy closed system values occur. In Bituminous shale environments limitation of organic matter can result in two ways 1. insufficient supply, 2. consumption of organic matter prior to entering the sediment by sulphate-reducing bacteria functioning in the overlying anoxic water. Hence limitation of sulphate reduction by organic carbon is promoted by conditions where the organic supply is limited and there is a great thickness of anoxic water. As a whole the Dunans Shale has a lower organic carbon content than the Posidonia Shales. When comparing



samples of the Dunans Shale with samples of the Posidonia Shales with similar organic carbon contents, the Dunans Clay samples tend to have the more negative  $\delta^{34}\text{S}$  values, suggesting that the open system anoxic water column was a more important element during the deposition of the Dunans Shale. The conclusion would therefore be that the anoxic water column under which the Dunans Shale was deposited was thicker than that in the Posidonia Shales.

To suggest that a model involving extensive stagnation is not applicable to the Posidonia Shales is at odds with the interpretation of Kùspert (1982). That interpretation is designed to explain the light  $\delta^{13}\text{C}$  values of both carbonate and organic carbon. There are several aspects of Kùsperts data that leave it open to re-interpretation. Two aspects in particular suggest that a model which supposes a smaller thickness of anoxic water might be at least equally applicable.

1. The relatively high pristane/phytane ratio
2. The negative correlation between  $\delta^{13}\text{C}$  organic and pristane+phytane/N-alkanes ratios.

The pristane/phytane ratios reported by Kùspert(1982) averaged about 1.45. Didyk et al (1978) have shown that the Pr/Ph ratio may be used as an indicator of the bottom water environment. A ratio  $<1$  indicate anaerobic conditions; values around 1 indicate conditions where the oxic/anoxic boundary is above but close to the



sediment surface and values  $>1$  oxic conditions. The ratios tend to show a general increase with thermal maturation. The value of 1.45 would suggest conditions with a smaller thickness of anoxic water, with the ratios increased slightly by thermal maturation. The slightly higher ratios of the Nurlingen borehole from the Urach-Kirchheim geothermal area would support this.

Küspert (1982) suggested no explanation for the negative correlation between the Pr+Ph/N-alkanes and the  $\delta^{13}\text{C}$  of the organic matter. One possible explanation would rest in the greater resistance of Pr+Ph to bacterial degradation compared to the N-alkanes. As sulphate reduction progresses the Pr+Ph/N-alkane ratio will increase. Progressive lightening of the  $\delta^{13}\text{C}$  organic carbon during degradation has been recognized by Sachett & Thompson (1963) for recent sediments and by Coleman and Raiswell (1981) for the Lias Jet Rock; this is due to the less reactive lipids having a lighter isotopic composition. Therefore both the increasing Pr+Ph/N-alkanes and the decreasing  $\delta^{13}\text{C}$  can be seen as the effect of the increasing degradation of organic matter during sulphate reduction. It would appear that the light  $^{13}\text{C}$  value of the organic carbon are not the effect of modification of the dissolved inorganic carbon pool but a result of early diagenetic alteration. The lighter carbonate carbon values result therefore from a mixing of primary and sulphate reduction carbonate with

the proportions being biased towards the sulphate reduction as the organic degradation increases (Irwin et al 1972).

The lack of iron in the Posidonia Shales may lead us to a possible explanation for origin of the limited anaerobic conditions in the overlying water.  $H_2S$  produced during sulphate reduction will be free to diffuse into the water column lowering the  $O_2$  concentration, creating a positive feed-back situation. The low oxygen concentration in the overlying water allows more metabolisable organic matter to enter the zone of sulphate reduction, which in turn will produce more  $H_2S$  which on diffusing back into the water column will further lower the  $O_2$  concentration. The extent of  $H_2S$  in the overlying water will be limited by the effects of currents mixing the the anoxic layer with the overlying oxygenated water. At times of greater current activity the whole anoxic layer may be removed, possibly leading to the poisoning of the water column and a mass mortality event. Such an event would then be followed by a period of oxic bottom conditions while the concentration of  $H_2S$  gradually built up. Such a sequence of events has been described by Kauffman(1978). Who explained it in terms of a minimal thickness of anoxic water.

7. Conclusions.

The Bituminous shale facies is characterized by high >2% pyrite sulphur content, due to the anoxic nature of the environment of deposition. They have variable  $\delta^{34}\text{S}$  pyrite values which depend on the extent of anoxia in the overlying water and the initial organic carbon concentration entering the zone of sulphate reduction.

The formation of pyrite in the Posidonia Shales is limited, in all but the most organic poor case, by the availability of iron indicated by the high D.O.P.s. The isotopic data suggests that the shales were deposited in conditions where the overlying water was anoxic for a short distance above sediment/water interface, and which anoxia was maintained by the diffusion of  $\text{H}_2\text{S}$  from the sediment. Sulphate reduction was limited in the sediment by the diffusion of sulphate which led to complete reduction of sulphate and isotopically heavy sulphide. Although not all the  $\text{H}_2\text{S}$  was able to precipitate at the point of formation some, would on encountering iron as it diffused up through the sediment, so enriching the sulphur isotopic composition of the iron sulphide.

In the Dunans Shale formation of pyrite may not have been limited in all cases by iron, but in some cases by its low organic carbon content. Its light  $\delta^{34}\text{S}$  values indicate that it was influenced more by open

system sulphate reduction in the water column than the Posidonia Shales. Sulphate reduction was limited in the sediment by the organic carbon, resulting from the lower carbon inputs and the consumption of organic in a greater thickness of anoxic water. Sulphate reduction did not proceed to completion and the heavier  $H_2S$  was not produced accounting for the lighter  $\delta^{34}S$  values.

It is possible therefore to divide Bituminous shales into two types:

1. Those with light  $<-28\text{‰}$   $\delta^{34}S$  values indicating sulphate reduction limited by organic carbon.
2. Those with heavy  $>-28\text{‰}$   $\delta^{34}S$  values indicating sulphate reduction limited by sulphate diffusion.

The former will generally be those with the lower organic carbon concentration and the greater extent of anoxic water. The latter will have the higher organic carbon concentrations and the lesser extent of anoxic water column. In all but the most organic poor cases the pyrite concentration in both types is limited by the availability of iron.

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Fig 4 Plot of pyrite sulphur vs organic carbon contents. Line marked 3 indicates mean C/S ratio of 3 for recent sediments (Berner and Raiswell 1983). • Posidonia Shale samples, ◐ Dunans Shale samples. Other lines indicate best fits for the two sets of data.



Table 1

## DUNANS SHALE DATA

SAMPLE	%S Pyrite	$\delta^{34}\text{S}$	%C Carb- onate	%C Organic	%Fe	DOP
SDS81/1	4.9	-28.6	0.96	5.16	3.13	0.58
SDS81/2	3.5	-33.5	0.23	4.62	0.75	0.80
SDS81/3	3.0	-20.4	0.07	10.42	0.59	0.82
SDS81/4	2.6	-33.1	0.04	5.83	1.02	0.69
SDS81/5	2.1	-40.9	0.05	4.06	1.29	0.59
SDS81/6	2.5	-39.5	0.09	4.17	0.88	0.71

Table 2

POSIDONIA SHALE DATA

SAMPLE	%S pyrite	δ34S	% Carb- onate	%C Organic onate	δ13C Carb- onate	δ13C Kerogen	%Fe (HCl)	D.O.P.
				HOLE 1002				
311	2.1	-24.9	32.7	6.4	+1.0	-28.9	N.D	N.D
319	2.3	-24.7	31.4	7.0	+0.4	-28.8	N.D	N.D
318	2.1	-20.6	46.8	6.0	-0.1	-29.2	N.D	N.D
320	2.0	-23.3	36.7	11.0	-0.6	-29.3	N.D	N.D
314	2.4	-24.5	41.3	8.8	+1.3	-27.9	N.D	N.D
312	2.1	-19.4	44.2	10.9	+1.4	-27.5	N.D	N.D
313	3.1	-25.6	35.6	8.6	+0.3	-27.7	N.D	N.D
315	2.4	-20.7	27.7	13.0	-1.7	-31.0	N.D	N.D
317	3.3	-21.3	19.4	11.1	-2.0	-31.7	N.D	N.D
316	3.2	-27.0	17.7	8.6	-1.0	-31.5	N.D	N.D
				HOLE 1005				
239	2.0	-16.6	38.2	8.9	+1.0	-29.1	0.36	0.83
237	2.2	-18.6	39.2	7.8	+1.2	-29.2	0.30	0.87
235	2.5	-17.6	39.3	6.8	+0.8	-29.4	0.35	0.86
233	2.5	-21.8	30.9	8.5	+1.1	-29.2	0.38	0.85
230	2.7	-33.0	31.6	4.2	+2.2	-28.0	0.48	0.83
228	2.4	-27.3	26.8	5.7	+2.1	-27.3	0.50	0.81
226	2.3	-25.2	31.1	12.7	+0.5	-28.7	0.33	0.86
224	1.6	-25.2	51.1	7.1	+0.4	-30.2	N.D	N.D
223	2.4	-22.0	26.2	17.6	-1.9	-31.8	0.29	0.88
221	2.3	-24.6	24.5	10.8	-3.1	-32.4	0.34	0.86
220	3.5	-23.4	15.6	10.8	-3.0	-32.4	0.43	0.88
217	2.3	-32.4	14.8	2.4	+1.6	-28.3	0.68	0.75

Fig 1    Section and sampling points from the Dunans  
         Shale, Staffin Bay Isle of Skye

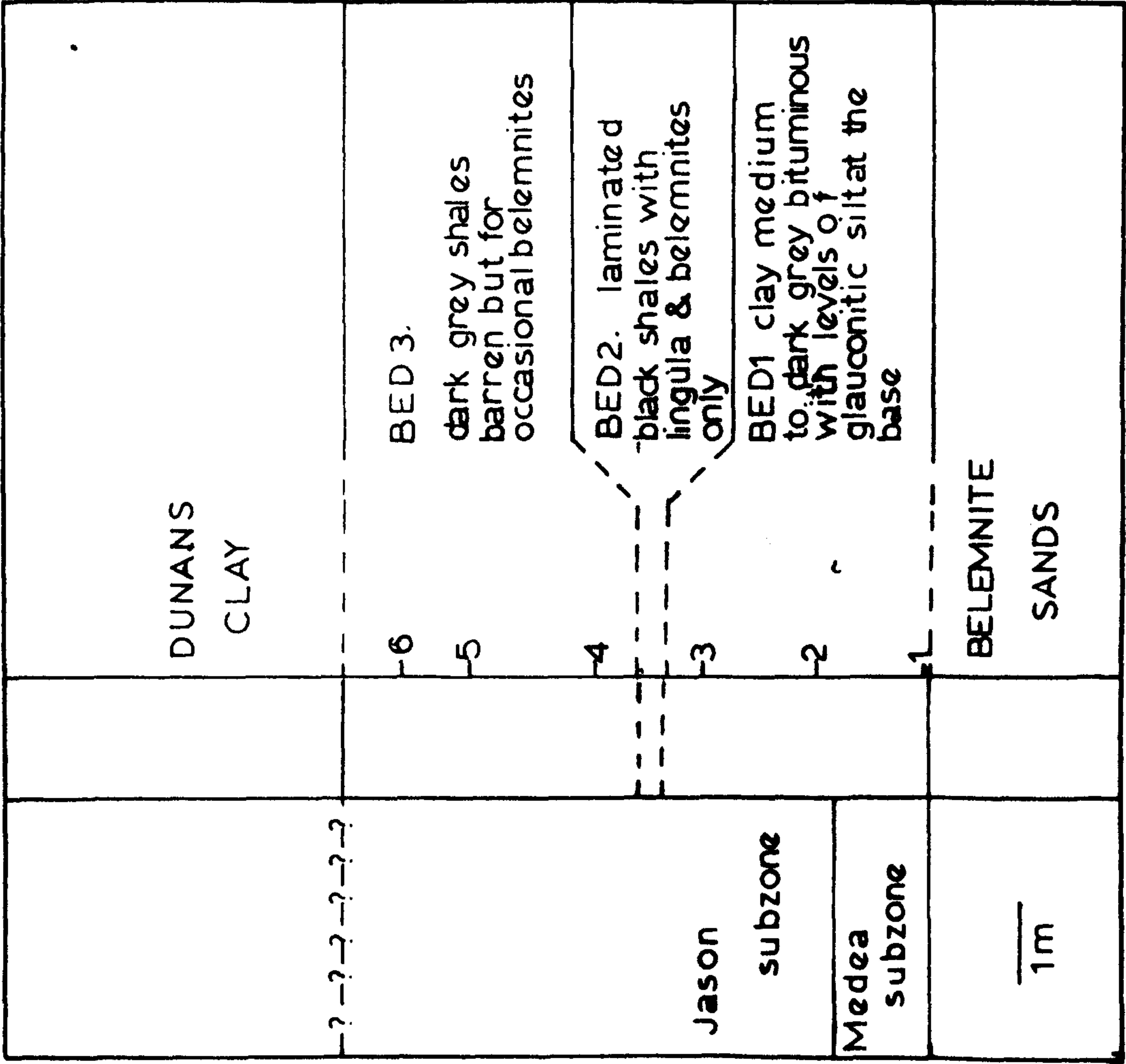


fig 1

Fig 2    Section and sampling points from the boreholes  
         in the Posidonia shales after Kűsper 1983.  
         Scale in metres



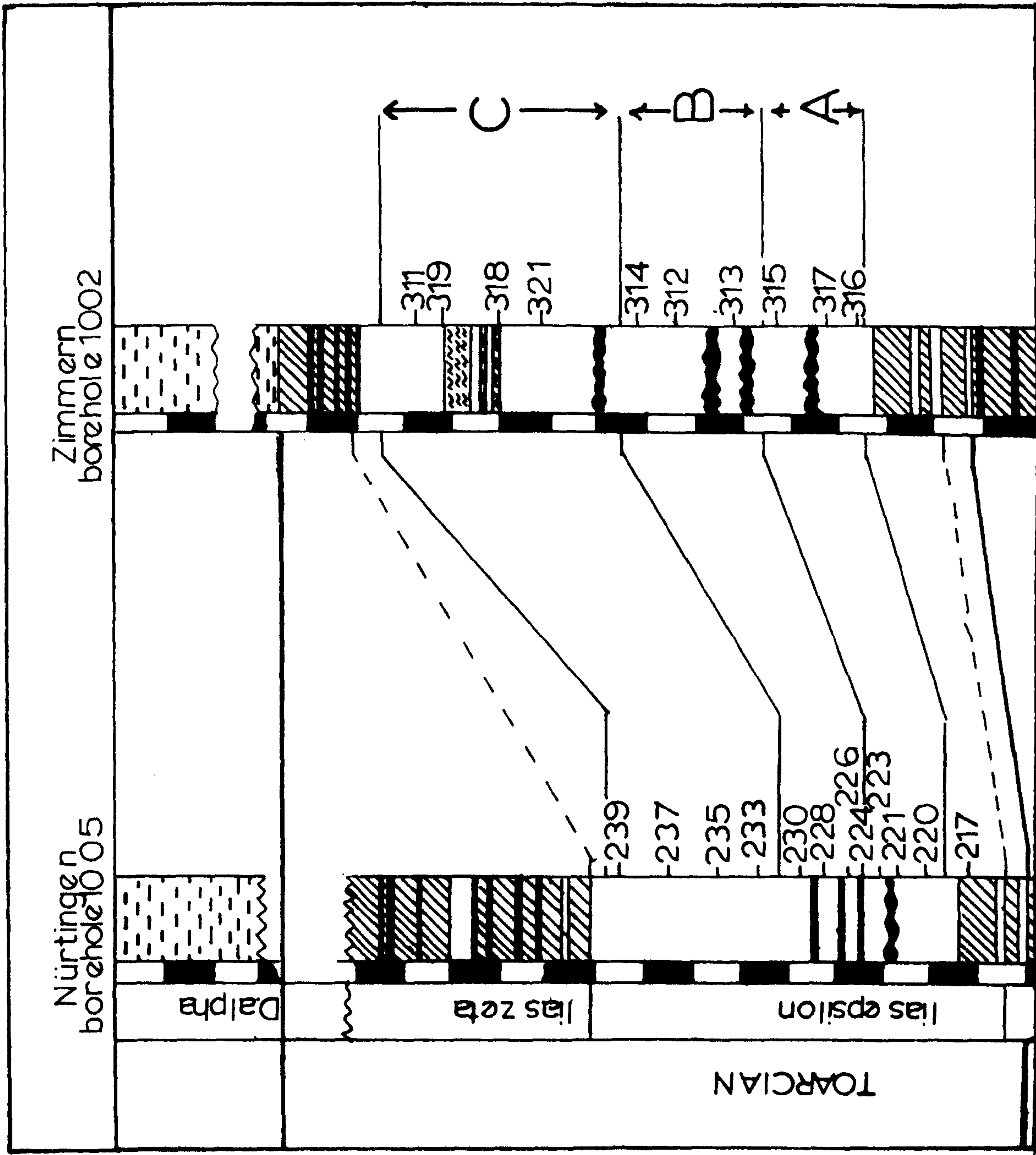


fig 2

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fig 3

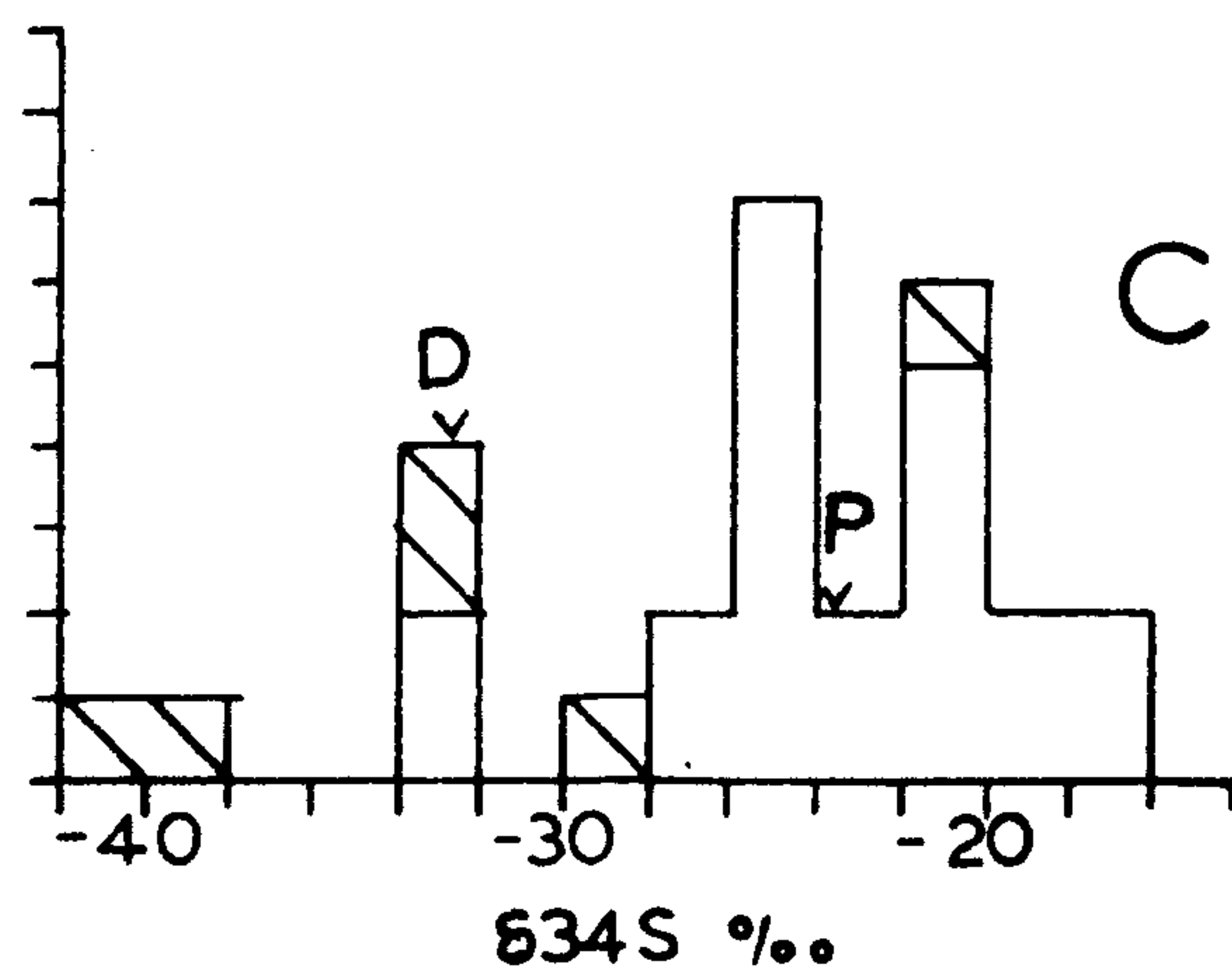
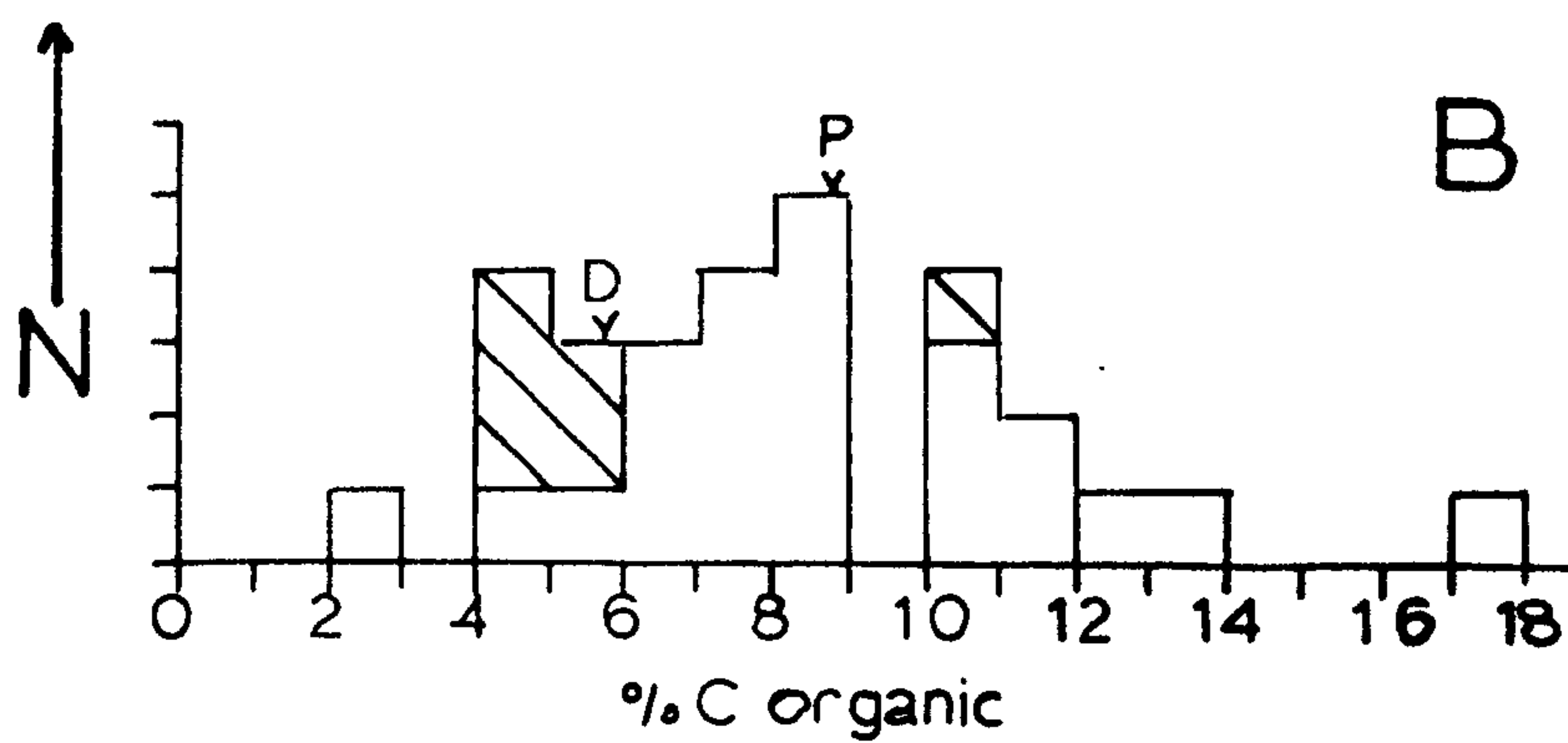
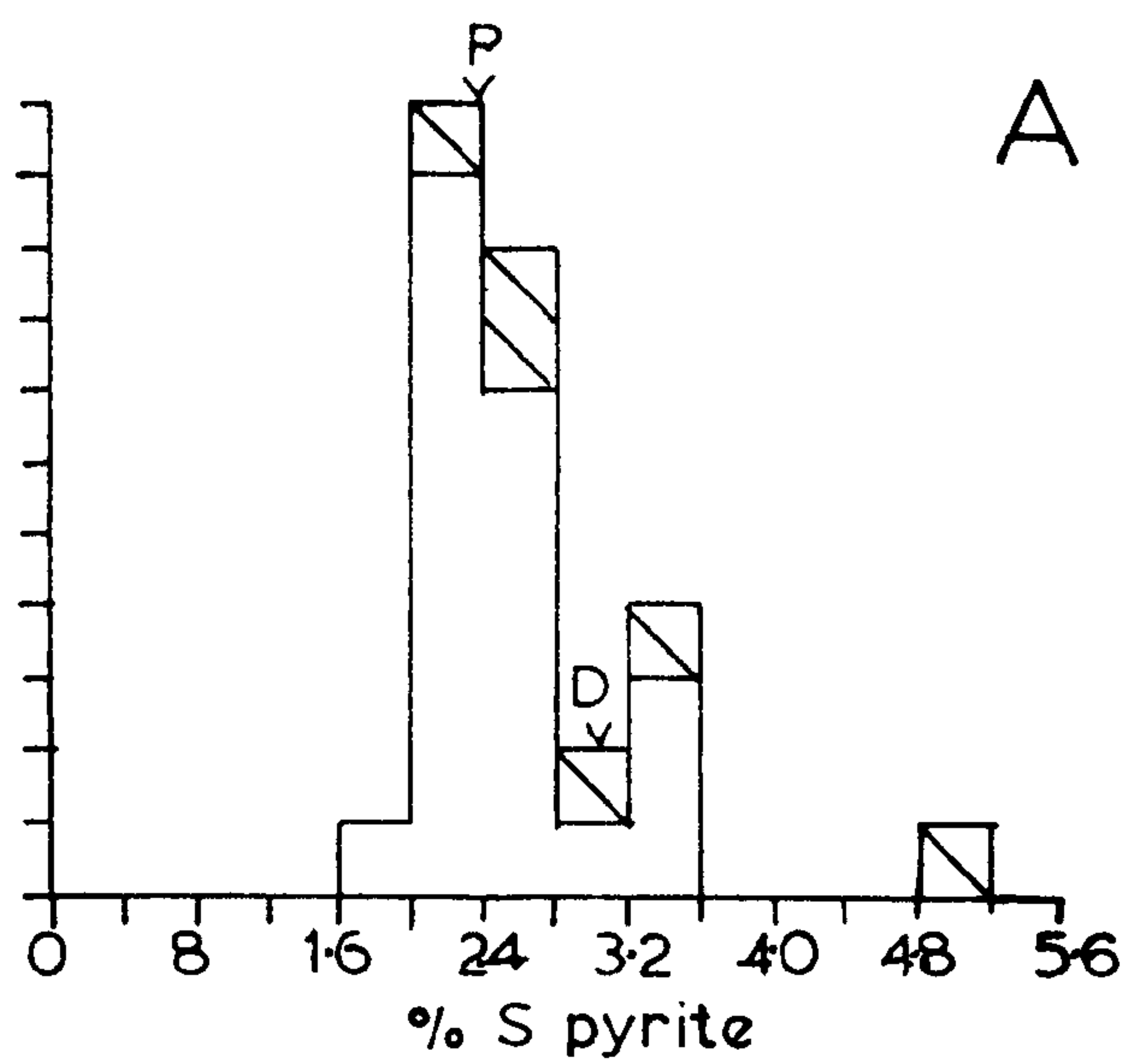
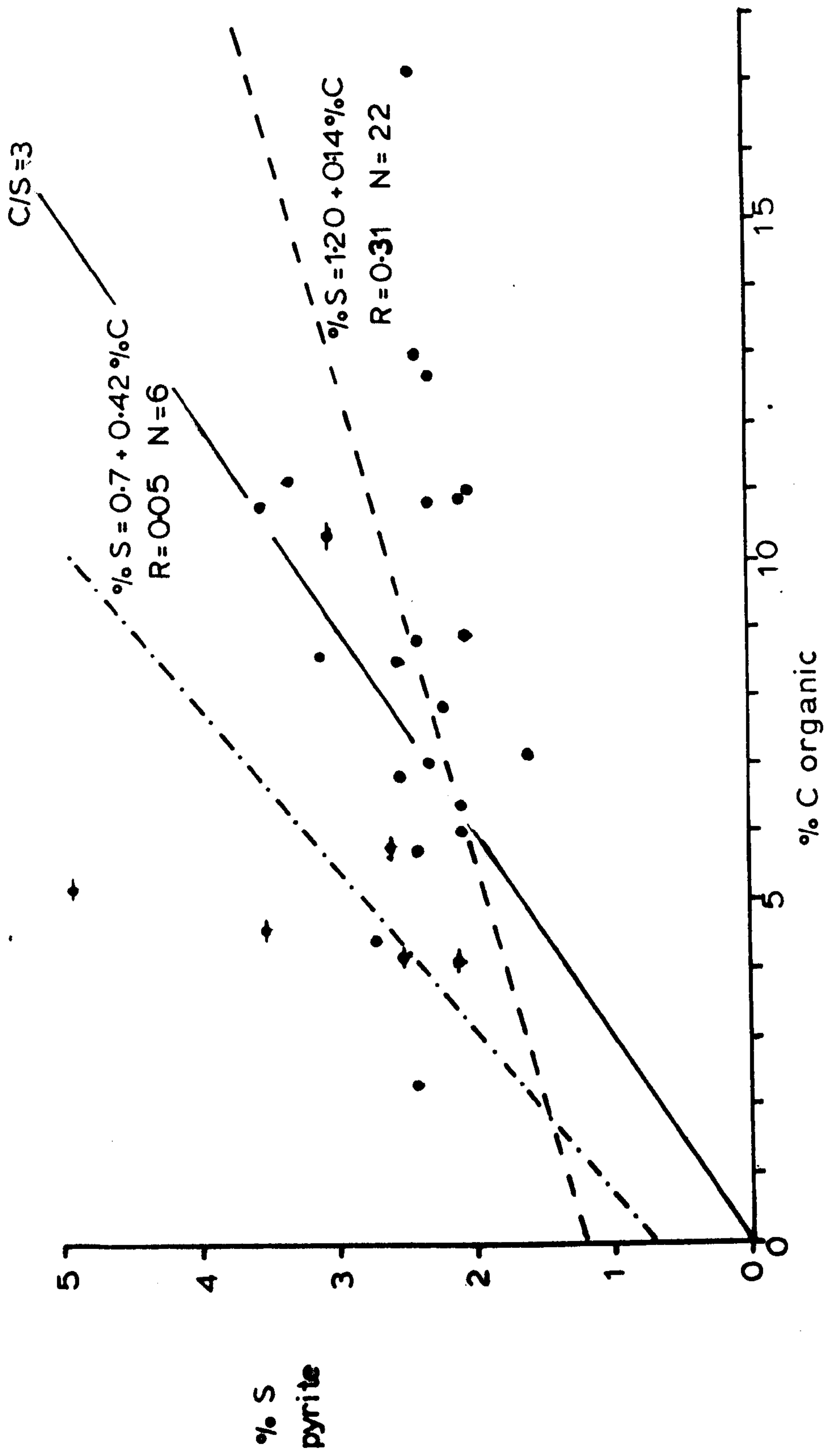


Fig 4 Plot of pyrite sulphur vs organic carbon contents. Line marked 3 indicates mean C/S ratio of 3 for recent sediments (Berner and Raiswell 1983). • Posidonia Shale samples , ♦ Dunans Shale samples. Other lines indicate best fits for the two sets of data.

Fig 4





Pyrite Formation In Jurassic Shales of Contrasting Biofacies.

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Abstract: The quantity and composition of organic matter passing into the hydrocarbon window is dependent on the extent of organic degradation occurring during early diagenesis. An important early diagenetic reaction in which organic matter is consumed is sulphate reduction. Relationships exist between pyrite sulphur (a product of sulphate reduction), organic carbon, and degree of pyritization of available iron, which can be used to help characterize the source rock potential. In Jurassic, marine, organic rich shales, these parameters are related to the environment of deposition, as indicated by biofacies analysis, and to variations in bottom water oxygenation, and supplies of organic carbon, sulphate and iron. The best preservation of organic matter, for reaction in subsequent diagenetic zones, does not necessarily occur in the most anoxic sediments, but in those in which sulphate reduction is limited by sulphate supply and not organic carbon. In the shales studied this is indicated by the most positive ( $>-28\text{‰}$ )  $\delta^{34}\text{S}$  values for fine grained pyrite.

Introduction

All marine organic-rich shales contain pyrite. Pyrite results from the anaerobic bacterial reduction of seawater sulphate, and the reaction of the sulphide formed with iron. These reactions follow the exhaustion of dissolved oxygen by aerobic bacteria, and both sets of reactions consume organic carbon compounds. The quantity, petrography and sulphur isotopic composition of pyrite formed depends on factors including oxygenation of depositional environment, the supply of organic metabolisable carbon, and the availability of

iron. These factors also affect shale's biofacies and early diagenetic history, and thus help determine whether it will carry enough reactive organic matter into later burial to make it a potential source rock.

Five Jurassic shale units were studied. Their stratigraphical (fig 1), sedimentological and palaeoecological attributes were reasonably well-known. We show that chemical aspects of pyrite formation differ in a predictable way among shales of different biofacies. We concentrate on fine grained dispersed pyrite in the shales. Elsewhere (Hudson 1982, Fisher, in prep) we describe the petrography and chemistry of pyrite associated with fossils as a replacement mineral or as a void filling, and of pyrite concretions. This also contributes to the characterization of shales as diagenetic systems, and carries the story later into the burial history.

### Biofacies Classification of Shales

Morris (1979,1980) studied several Jurassic shales and generalized from earlier work to erect a three fold classification of shales based on types of bivalve mollusc present. These are the dominant macrofossils in Jurassic (and many other) shales and can be referred to different groups in terms of mode of life (infaunal, epifaunal) and feeding (deposit feeders, suspension feeders). Morris showed that his classification

corresponded with other factors such as degree of preservation of lamination versus bioturbation. We have characterized our shales on a Morris triangular plot (fig 2).

### 1. Normal Facies (Dunans Clay and Upper Oxford Clay)

A mixed fauna of infaunal and epifaunal types, with both shallow and deep burrowers, but with deposit feeders representing <20% of the fauna. Abundant Chondrites and other horizontal burrows. Bioturbation destroys primary lamination. In this facies the benthic waters were well oxygenated and the action of burrowing organisms allowed oxic conditions to persist for several tens of centimetres in the sediment.

### 2. Restricted Facies (Lower Oxford Clay)

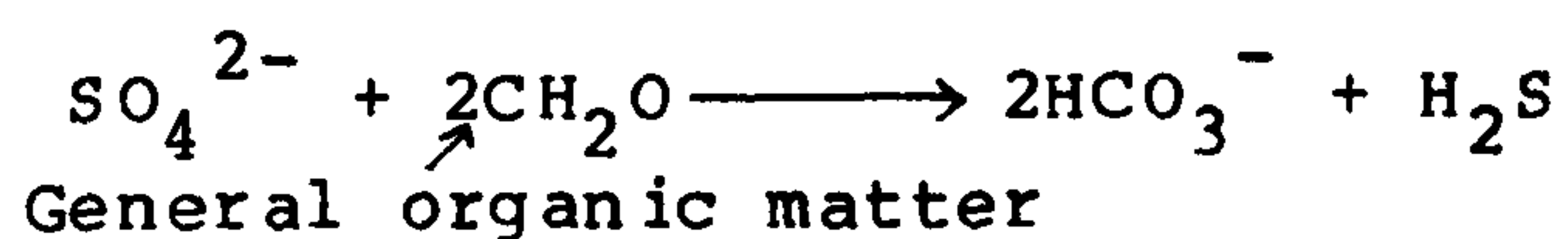
Dominated by infaunal deposit feeders, with few infaunal suspension feeders, but epifaunal suspension feeders are often numerous and may have lived attached to floating wood or to weed (Duff 1975). Trace fossils are not abundant, only occasional Chondrites and horizontal pyrite-filled burrows. The presence of benthic organisms indicates oxygenated bottom waters, although many forms are tolerant of low oxygen conditions. The mobile infaunal deposit feeders totally rework the sediment producing a somewhat soupy sediment surface (Aller 1977, Rhoads 1963, Rhoads and Young 1970). Below this layer the sediment rapidly becomes anoxic.

### 3. Bituminous Facies (Posidonia Shales and Dunans Shales).

The fauna comprises almost entirely epifaunal suspension feeders with infaunal types rare or absent. Many epifaunal types may or may not have been truly benthic (Kauffman 1978, cf Duff 1975). Trace fossils are absent except at occasional horizons, and sedimentary lamination is well preserved. The lack of benthic organisms suggests that the bottom water was anoxic. The extent of anoxic water could be anything from a few centimetres to several hundred meters, and is a much debated quantity (see Morris 1980, Kauffman 1978, Seilacher 1982)

#### Controls of Pyrite Formation and Sulphate Reduction

The formation of pyrite in marine sediments is due to the action of sulphate-reducing bacteria on seawater sulphate to form sulphide, which reacts with iron to form pyrite, either directly or via a monosulphide precursor (Goldhaber and Kaplan 1974). The reactions may be summarized as follows;





The iron "monosulphide" (mackinawite) may proceed to pyrite via the addition of elemental sulphur. If the reaction proceeds via greigite ( $\text{Fe}_3\text{S}_4$ ) the characteristic framboidal texture results (Sweeney & Kaplan 1973). The formation of greigite from mackinawite is an oxidation reaction, suggesting that the formation of framboids requires conditions which are not totally reducing. Hudson (1982) noted that the more oxic Upper Oxford Clay contained larger framboids than the anoxic Posidonia Shales.

There are four prerequisites for the formation of pyrite:

1. Anoxic condition in which the sulphate-reducing bacteria may function, as they are obligate anaerobes. It is not necessary for the overlying water column to be anoxic, as sulphate reduction may occur in anoxic sediments beneath a layer of oxic sediment. Pyrite formation is also seen to occur in generally oxidising sediments, within reducing microenvironments, e.g. disused burrows or faecal pellets, or enclosed voids such as foram tests or ammonite chambers (Kaplan et al 1963, Hudson 1982)
2. Sulphate. The chief source in marine sediments is seawater. If reduction occurs within the water column then sulphate-reducing bacteria are in contact with an essentially infinite reservoir. Similarly in oxic sediments bioturbation and mixing serve to keep the



concentrations in that sediment layer close to that of seawater. Beneath such a mixed zone, sulphate is supplied to the sediment by diffusion, the gradient being controlled by the rate of sulphate reduction (Berner 1980)

3. Organic matter is necessary as the material on which sulphate-reducing bacteria feed. Various laboratory experiments indicate that the rate of sulphate reduction is dependent both on the quantity and quality of organic matter; high rates of reduction are associated with large concentrations of organic matter (Harrison and Thode 1958). A general covariance between pyrite sulphur content and organic matter has been noted by several authors (Berner 1970, Sweeney 1972, Goldhaber and Kaplan 1974). Initially large concentrations of organic matter give rise to larger quantities of pyrite sulphur, and, if the metabolised organic matter is a constant proportion of the total initial organic matter entering the sulphate reduction zone, then a linear correlation between pyrite sulphur and organic carbon results. Sweeney (1972) produced a compilation for recent sediments and found a C/S ratio of about 3. In euxinic conditions C/S ratios consistently less than 3 and regression lines with positive intercepts on the S axis have been demonstrated (Leventhal 1983, Berner & Raiswell 1983). This is due to larger proportion of metabolisable organic matter entering the sulphate

reduction zone and a decoupling of that organic matter from its complementary sulphide. Aerobic degradation of organic matter, prior to entry into the sulphate reduction zone, reduces the total and the metabolisable proportion of organic matter. Therefore the more aerobic the conditions the less metabolisable organic matter enters the sulphate reduction zone (Zolnay 1971).

4. Iron is necessary for the conversion of  $H_2S$  into iron sulphide. Iron is supplied to the sediment in detrital minerals and as iron oxide coatings on grains, and is in the ferric form.  $H_2S$  may react in situ with ferric iron and simultaneously reduce it and precipitate it as iron sulphide (Berner

1969). When all in situ iron is consumed the  $H_2S$  will be free to diffuse from the site of reduction, unless iron is available to diffuse in, this only being so when it is in the ferrous form. If conditions are totally reducing then iron will be free to diffuse. In conditions that are not totally anoxic, such as the surface layers of Normal shales,  $H_2S$  may be lost into oxidizing environments.

If sufficient organic carbon and sulphate are present to maintain high  $H_2S$  concentrations then the amount of pyrite formed will be limited by the iron present. Berner (1970) used the parameter Degree Of Pyritization (D.O.P.), defined as:

$$\text{D.O.P.} = \frac{\% \text{Fe as Pyrite}}{\% \text{Fe as pyrite} + \% \text{Fe HCl}}$$

%Fe HCl is the amount of iron liberated on treatment with hot conc. HCl, and is a measure of the Fe still available which would be reactive to H<sub>2</sub>S. If pyrite formation is limited by Fe then D.O.P. will approach 1.

Sulphate reduction is not affected by the availability of iron, only by sulphate and organic carbon. When iron is limited, sulphate reduction will continue until either sulphate or metabolisable organic matter is exhausted. The result of this is that H<sub>2</sub>S is produced which diffuses away from the site of reduction and into the overlying sediment or water column. Free H<sub>2</sub>S may react with other minerals or organic compounds and produce sulphides other than pyrite.

### Controls of $\delta^{34}\text{S}$ variation

Three factors may affect the  $\delta^{34}\text{S}$  value of fine grained pyrite formed in shales:

1. The natural fractionation between sulphate and the sulphide produced from it.
2. The  $\delta^{34}\text{S}$  value of the sulphate. As the  $\delta^{34}\text{S}$  composition of seawater has varied with time it is often useful, when comparing data from different geological periods, to refer to S isotopic data in terms of its difference from contemporary seawater ( $\Delta^{34}\text{S}$ ). Jurassic seawater had a composition of +16‰ (Claypool et al

1980). If the environment of sulphate reduction becomes closed or partially closed to the access of sulphate the value will change, becoming enriched in  $^{34}\text{S}$  due to the preferential removal of light sulphide.

3. The proportions of the total sulphide formed at each stage of burial, either within a closed or open system.

Fractionation factors for bacterial sulphate reduction have been experimentally investigated by several authors (a review is given by Chambers & Trudinger 1979). Experiments show fractionations between +3 and -46‰ and indicate that the greatest fractionations are obtained at the slowest specific rates of reduction. It has been suggested that at extremely slow rates of reduction fractionations may approach equilibrium values, -74‰ at 25° (Tudge & Thode 1958, Trudinger & Chambers 1973). Chambers and Trudinger (1979) show that fractionations in recent sediments range between -34 and -59‰, with a mean of -50‰, and for reduction occurring in anoxic water columns -43‰. These values are more negative than those found by experiment. This may be due to slower specific rates of reduction in sediments, or to the addition of isotopically light sulphate by the reoxidation of sulphide.

If sulphate reduction takes place in an open system in contact with the seawater reservoir i.e. in an anoxic water column or the bioturbated and mixed



sediment surface, the sulphate reservoir is essentially infinite and the removal of light sulphide does not significantly alter the isotopic composition. On further burial sulphate is supplied by diffusion and the removal of light sulphide enriches the sulphate in  $^{34}\text{S}$ .

Goldhaber and Kaplan (1980) have demonstrated that the  $^{32}\text{S}$  gradient is enhanced by its preferential removal and that on total reduction the resulting sulphide has a displacement from seawater  $\Delta^{34}\text{S}$  of  $-25\text{‰}$  and not  $0\text{‰}$  as would otherwise be expected.

There are therefore two zones in which sulphate is reduced;

1. An open system zone in an anoxic water column or bioturbated sediment with sulphide forming at  $\Delta^{34}\text{S}$  of about  $-50\text{‰}$ .
2. A partially closed system where sulphate is supplied by diffusion and sulphide forms at up to  $\Delta^{34}\text{S} = -25\text{‰}$ .

Goldhaber and Kaplan (1980), using a similar system, modeled the isotopic composition of pyrite from the Gulf of California. The majority of sulphate reduction takes place in the surface layers of the sediment, biasing the result towards the open system value. The addition of sulphide in the diffusion zone is partly dependent on the concentration of organic matter. If organic matter is exhausted prior to sulphate the most positive  $^{34}\text{S}$  values will not be reached. It can be demonstrated from the equations of Berner (1980) that, when the



metabolisable organic matter is more than sufficient to satisfy the sulphate in the diffusion zone, the quantity of sulphide formed is dependent solely on the diffusivity of the sediment and the concentration of sulphate in the overlying water. Therefore for sediments with similar diffusive properties the quantity of sulphide formed in the zone of diffusion is more or less constant and of the order of 0.5% S if trapped as pyrite.

When iron is limiting, excess  $H_2S$  is free to diffuse from the site of reduction into overlying sediment and form iron sulphides. The isotopic composition of the  $H_2S$  is dependent on the extent to which the sulphate is reduced, and therefore on whether sulphate or organic matter is limiting. In the former case the heavier values result.

### Results

The results of pyrite sulphur,  $\delta^{34}S$ , organic carbon and D.O.P. are summarized in the histograms in fig 3. Details of sampling and analyses for each unit will be presented elsewhere.

1. Normal facies. (Dunans Clay and Upper Oxford Clay)  
Low organic carbon contents and D.O.P.s suggest that pyrite formation and sulphate reduction were limited by organic carbon. The light  $\delta^{34}S$  values suggest that the

majority of sulphide was produced in the the surface bioturbated layer and that the organic carbon content was insufficient to continue sulphate reduction to any extent in the zone of diffusion.

### 2. Restricted facies (Lower Oxford Clay)

The D.O.P.s suggest that iron was not limiting in pyrite formation. The greater organic carbon input and lower bottom water oxygenation prolonged sulphate reduction into the zone of diffusion, as indicated by the more positive  $\delta^{34}\text{S}$  values. The formation of pyrite was probably ultimately limited by the diffusion of sulphate, and hence the large range of organic carbon concentrations are not accompanied by a correspondingly large variation in pyrite sulphur. The limitation by sulphate is supported by the isotopes whose heavy values suggest that sulphate reduction continued to completion.

### 3. Bituminous facies

**Posidonia Shales:** The high D.O.P.s ( $>.8$ ) indicate that pyrite formation was limited by iron. The heavier isotopic composition (mean  $\delta^{34}\text{S} = -24\%$ ) show a significant contribution of closed system reduction.

**Dunans Shale:** The greater range of D.O.P.s are probably the result of weathering producing iron oxides which give spuriously large %Fe HCl and low D.O.P.s. The pyrite sulphur values indicate that during deposition more iron was available, as the most pyrite rich samples have a %Fe pyrite greater than the total %Fe pyrite+%Fe

HCl in any of the Posidonia Shale samples. The  $\delta^{34}\text{S}$  values (mean  $-34\text{‰}$ ) show a domination by open system reduction, and suggest that sulphate reduction was limited by the supply of metabolisable organic matter.

### Relationship Between Pyrite Sulphur and Organic Carbon

Fig 4 shows a plot of pyrite sulphur vs organic carbon for the various shales. The mean C/S ratio of 3.2 is close to that found in recent sediments. Taken separately only the data for the Normal facies shows a significant positive correlation. This is probably due it being the only one in which organic carbon limits pyrite formation.

For the Restricted facies the most organic rich samples do not show correspondingly high sulphur values. This is due to the limitation of pyrite formation by sulphate, so that the more organic-rich samples preserve their excess carbon through the sulphate reduction zone.

The Bituminous facies can be divided into two.

1. The Posidonia Shales show mean to high C/S ratios. As pyrite formation is limited by iron the pyrite sulphur content represents only a fraction of the total sulphate reduced, raising the C/S ratio. The heavier  $\delta^{34}\text{S}$  values (see below) suggest that sulphate reduction was limited by diffusion, allowing excess organic matter to survive,

further raising the C/S ratio.

2. The Dunans Shale shows the lower C/S ratios associated with deposition beneath an anoxic water column. This is probably due to two factors a) Sulphate reduction was limited by organic carbon; indicated by the lighter  $\delta^{34}\text{S}$  values. b) More iron was available to precipitate the majority of  $\text{H}_2\text{S}$  formed and in some cases possibly all.

It is easy to wonder why the mean C/S ratio of all samples is so close to that of Sweeney (1972). The regression line on the S vs C plot is controlled mainly by the Normal and Restricted shales. For the Restricted shales, although sulphate is ultimately limiting, the majority of sulphate is reduced in the first ten or so centimetres of the sediment (Goldhaber and Kaplan 1974) in an essentially open system. Therefore it is only the samples with the extreme organic carbon contents which show noticeable digressions from the Sweeney line.

### Relationship of Pyrite Sulphur and $\delta^{34}\text{S}$ for the Three Biofacies

Fig 5 demonstrates the fields of the three biofacies on a Pyrite sulphur/ $\delta^{34}\text{S}$  plot, from the data obtained in the study. For the Normal facies the limitation by organic carbon and the formation of pyrite in the zone of bioturbation, position them in the low  $\delta^{34}\text{S}$  and most negative  $\delta^{34}\text{S}$  portion of the plot. The extremely light



values found in some samples ( $\Delta^{34}\text{S}$  down to  $-58\%$ ) are probably due to the recycling of light sulphide in the mixed oxic/anoxic conditions. Such lowering of the sulphate isotopic composition has been postulated from studies of structural sulphate in francolite (Benmore et al 1983) showing depletion in  $^{34}\text{S}$  of up to  $10\%$ .

In the Restricted facies the prolonged sulphate reduction and the ultimate limitation by sulphate diffusion produces greater quantities of pyrite with the most enriched  $\delta^{34}\text{S}$  values.

On the plot the Bituminous shales have been divided into Type 1 and Type 2. In both cases the anoxic overlying water allows the formation of greater quantities of pyrite, whose formation is most commonly limited by iron. For Type 1 Bituminous shales (Dunans Shale) the lighter  $\delta^{34}\text{S}$  values result from sulphate reduction being limited by organic carbon. The lower organic carbon input and probably more extensive anoxic conditions lead to the exhaustion of the organic matter before sulphate reduction in the zone of diffusion is complete and heavier  $\delta^{34}\text{S}$  values do not result.

In Type 2 Bituminous shales (Posidonia Shales), the greater quantity of organic matter and lesser extent of anoxic water allow large quantities of organic matter to enter the zone of diffusion, and reduction of sulphate diffusing in to the sediment goes to completion. The heavier  $\text{H}_2\text{S}$  diffuses back up through the sediment where



some is precipitated as pyrite, enriching its  $\delta^{34}\text{S}$  value. As a larger proportion of sulphate is reduced in the open system anoxic water column than in the bioturbated sediment of the Restricted facies, due to the larger proportion of metabolisable organic matter entering the sulphate reduction zone, the  $\delta^{34}\text{S}$  values in the Type 2 Bituminous shales are biased slightly more towards the open system values.

### Conclusions

Fig 6 summarizes some of the environmental variations, the production of pyrite, and the theoretical  $\Delta^{34}\text{S}$  values produced.

In the Normal facies the formation of pyrite is limited by the oxic nature of the sediments. Pyrite is formed mainly in the zone of bioturbation and mixing, and in the more organic-rich sediments continues slightly into the zone of diffusion. The resulting pyrite content is low and the  $\Delta^{34}\text{S}$  values approach their most negative.

In Restricted shales the lower degree of oxygenation allows a greater proportion of metabolisable organic matter to enter the sediment. The zone of bioturbation is less extensive as deep burrowers are not present. Sulphate reduction continues to greater depths in the zone of diffusion and is limited by sulphate, so heavier

isotopic values result. The extent of the zone of diffusion is dependent on the rate of sulphate reduction, which is tied to the input of organic matter and the rate of sedimentation (Berner 1980).

In Bituminous shale facies the  $O_2/H_2S$  boundary crosses the sediment water interface, and this facies would include environments with anything from a few centimetres to several hundred metres of anoxic water. Sulphate reduction occurs within the anoxic water column with open system  $\Delta^{34}S$  values and within the sediment where sulphate is supplied by diffusion. The formation of pyrite is limited by the availability of iron, and hence free  $H_2S$  may be produced in the sediment and can diffuse upwards into the overlying sediment and water column. Sulphate reduction is limited by either sulphate or organic carbon, and is balanced by the input of organic matter and the extent of anoxic water. Where organic input is lower and the anoxic water column more extensive organic matter can become exhausted by anaerobic degradation prior to entry into the zone of diffusion and, hence, heavier sulphide is not produced. This occurs in Type 1 Bituminous shales. Where organic input is greater and the extent of anoxic water less, metabolisable organic matter survives and enters the sediment and the zone of diffusion. Subsequent reduction is limited by sulphate diffusion and the pyrite becomes enriched in  $^{34}S$ . This is the sequence of events in Type

## 2 Bituminous Shales.

When diffusion limits sulphate reduction more organic matter is preserved through the sulphate reduction zone. This occurs generally in the Restricted and Type 2 Bituminous shale environments. In the Normal and Type 1 Bituminous facies organic matter is limited either by, in the former case, extensive oxic degradation, or, in the latter, by anaerobic degradation. These correspond to two of the unfavourable cases for organic matter burial discussed by Curtis (1977). On the other hand the restricted and Type 2 Bituminous shales are favoured as source rocks. The lateral equivalents of the Posidonia Shales are the source rocks for oil in the Jurassic of the Paris Basin (Tissot et al 1971). The Lower Oxford Clay of the Midlands would no doubt be an excellent source rock except that it is immature. As it is, its organic carbon content (and other favourable properties) support a major brick industry (Callomon 1968).

It can be seen that the classification of Morris (1979,1980) represents distinct environments of shale deposition, which have correspondingly different early diagenetic histories resulting in radically different organic preservation and pyrite formation. Studies reported here have some advantage over other ways of characterizing shales. Unlike most biofacies schemes, they are not limited by the stratigraphic range of

particular fossils. In that they rely on the fine grained component, they do not depend on collecting macrofossils or finding concretions: they are easily carried out on core material. The relationships described should be fairly independent of maturity. They can be easily combined with palynofacies analyses (Tyson, in prep) or with kerogen-typing and maturity analyses.

Acknowledgements.

The work for this paper was undertaken during the tenure of a N.E.R.C. C.A.S.E studentship with the Institute of Geological Sciences. We should like to thank Dr M.L.Coleman who co-supervised the project and the staff of the stable isotope facility at Grays Inn Road. This paper is published with the permission of the Director, Institute of Geological Sciences (N.E.R.C.). We would like to thank Wölfgang Küsspert of Tübingen University who supplied samples and data for the Posidonia Shales, London Brick Company PLC. and John Horrell for permission to collect from their pits, Dr Keith Duff and Dave Martill who assisted in the sample collecting, and Sue Button who drew the diagrams.

Fig 1. Stratigraphic distribution of formations studied.

Fig 2. Shales classified by bivalve ecology. After Morris (1980).

Fig 3. Variation in %S pyrite,  $\delta^{34}\text{S}$ , %C organic, and D.O.P. . Dashed lines indicate movement of the means between units. Shales grouped in order of decreasing pyrite content.


Fig 4. Graph of %S pyrite vs %C organic showing fields of the three biofacies. Best fit and mean C/S ratio lines plotted.

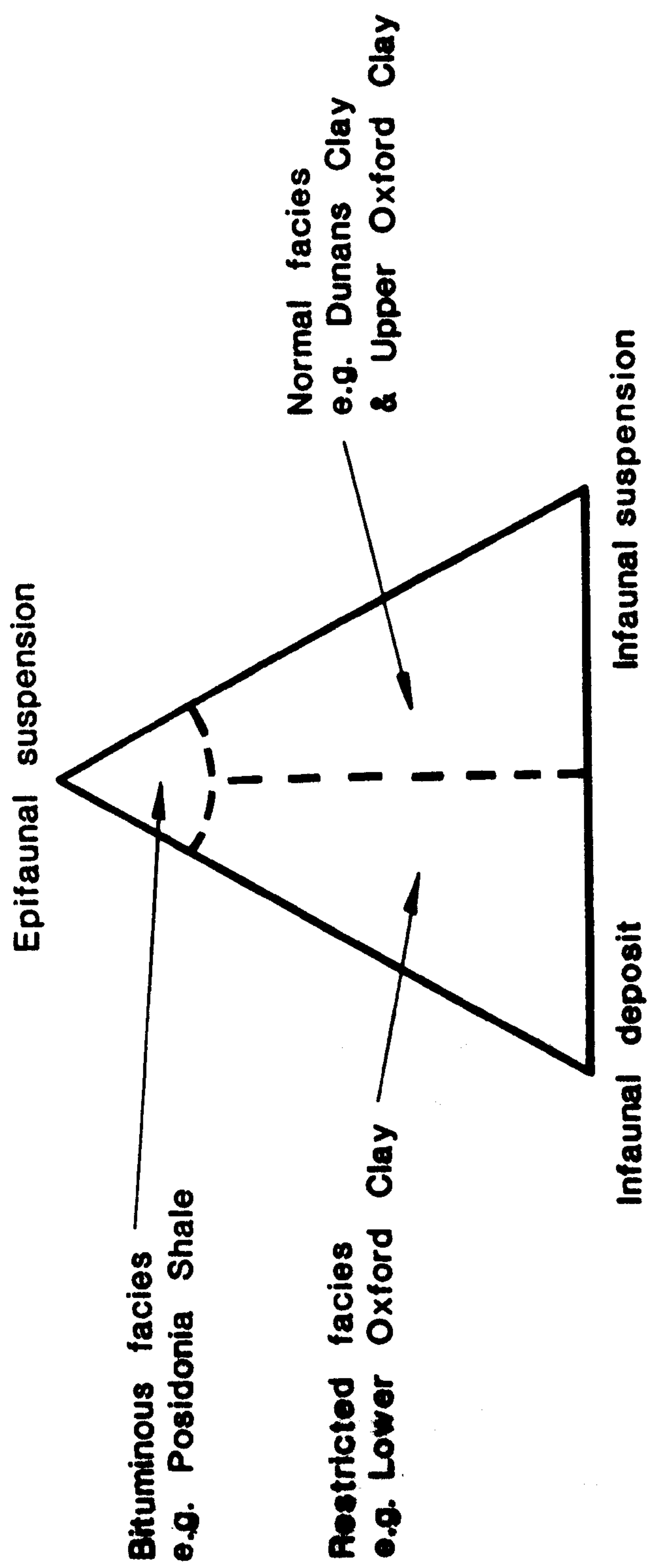
Fig 5. Distribution of biofacies on %S vs  $\delta^{34}\text{S}$  plot from data.  $\Delta^{34}\text{S}$  values indicated for comparison with shales of other geological periods.

Fig 6. Environmental variations between three biofacies. Plot indicates controlling factors for pyrite formation in each biofacies.



STRATIGRAPHIC CLASSIFICATION OF FORMATIONS STUDIED

J U R A S S I C	U P P E R P A R T		ENGLAND	SKYE	S. GERMANY	M A L M
			U. Oxford Clay	Dunans Clay		
	M I D D L E	Oxfordian				D O G G E R
			L. Oxford Clay	Dunans Shale		
		Callovian				
		Bathonian				
	L O W E R	Bajocian				L I A S
		Aalenian				
	L O W E R	Toarcian			Posidonia Shales ζ ε δ	L I A S
		Pliensbachian				
		Sinemurian				
		Hettangian				



SHALES CLASSIFIED BY BIVALVE ECOLOGY ( After Morris 1980 )

Fig 3. Variation in  $\delta S$  pyrite,  $\delta^{34}S$ ,  $\delta^{13}C$  organic, and D.O.P. . Dashed lines indicate movement of the means between units. Shales grouped in order of decreasing pyrite content.

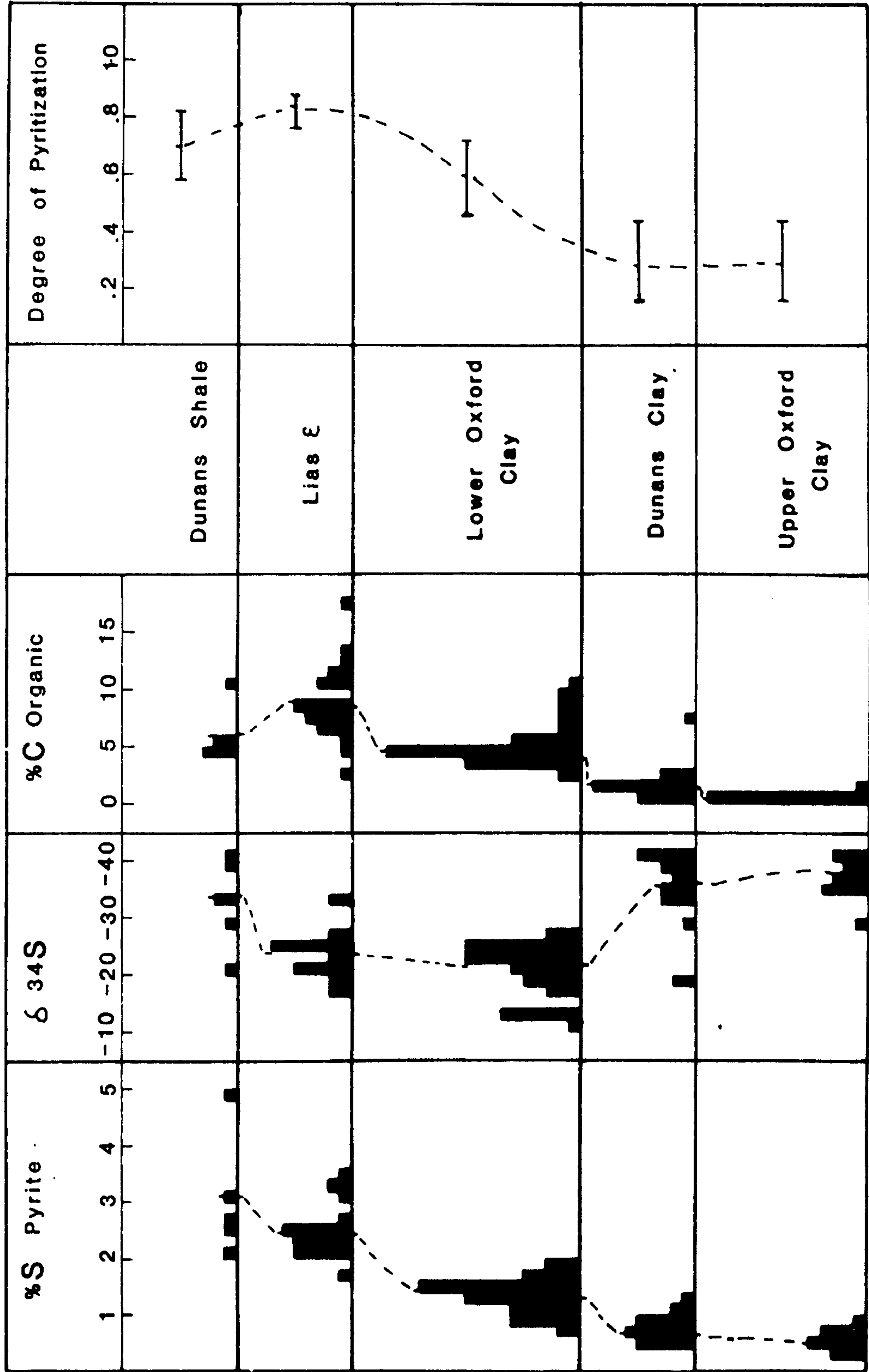


Fig 4. Graph of %S pyrite vs %C organic showing fields of the three biofacies. Best fit and mean C/S ratio lines plotted.



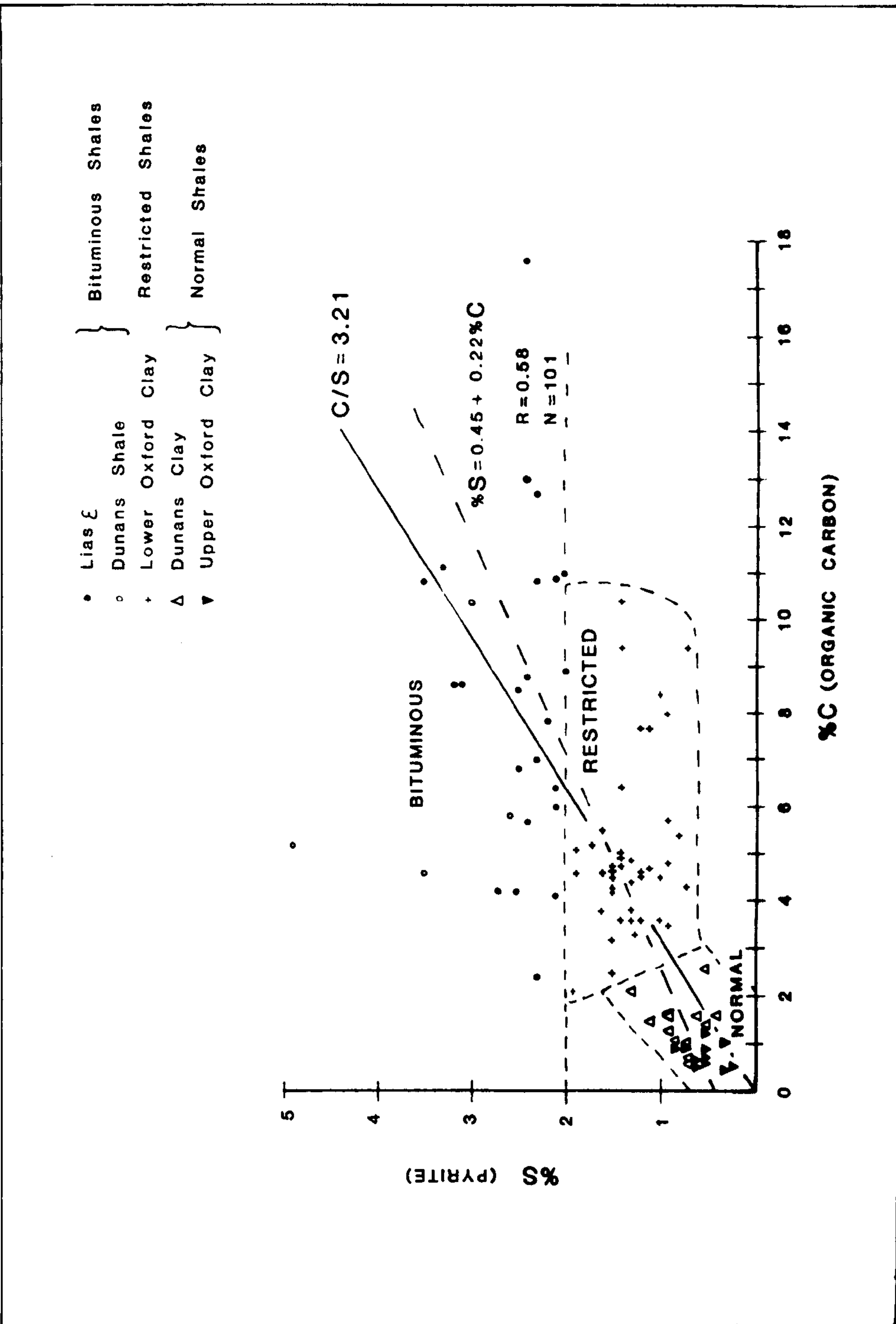


Fig 5. Distribution of biofacies on  $\delta S$  Vs  $\delta^{34}S$  plot from data.  $\Delta^{34}S$  values indicated for comparison with shales of other geological periods.

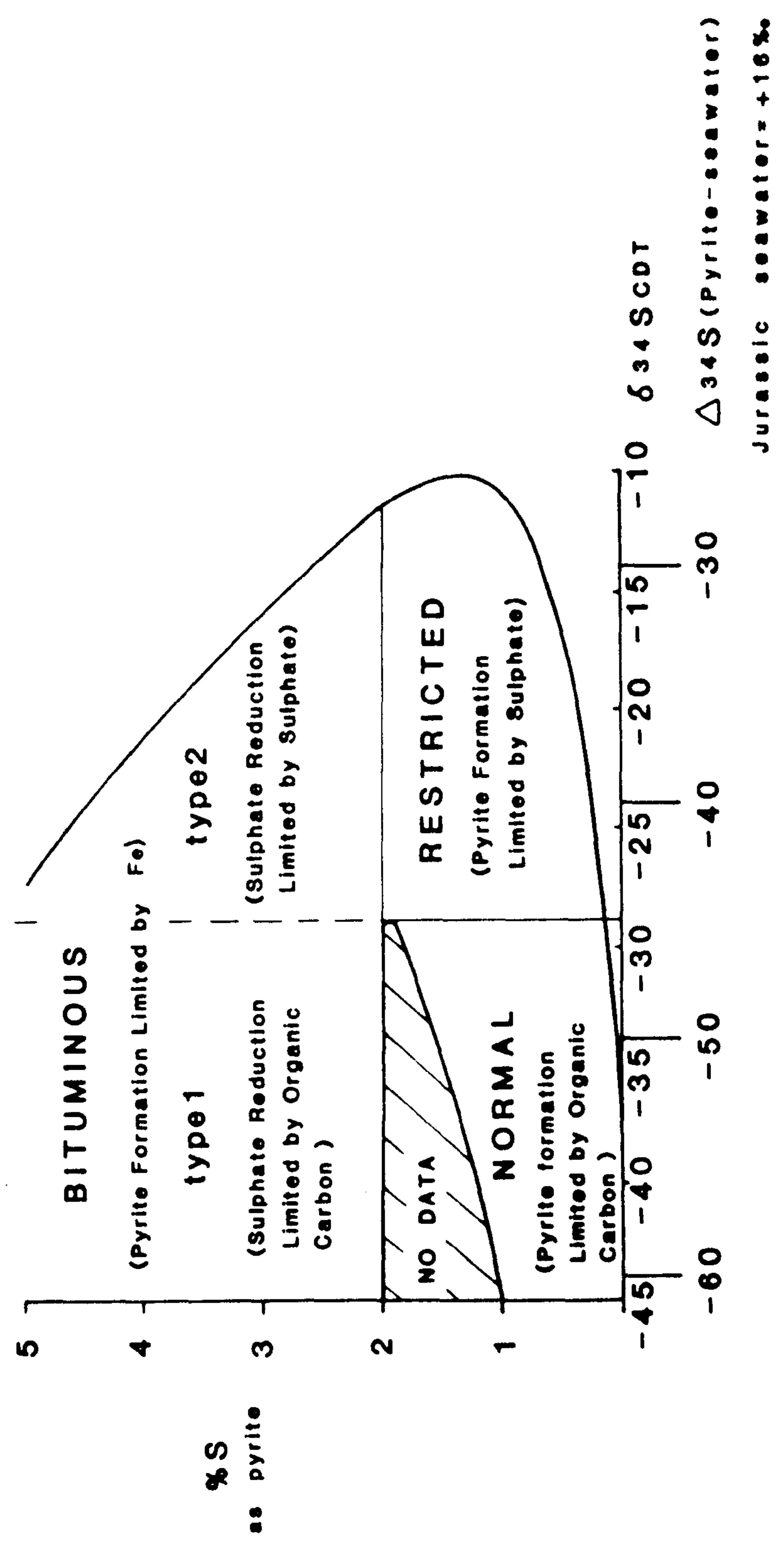
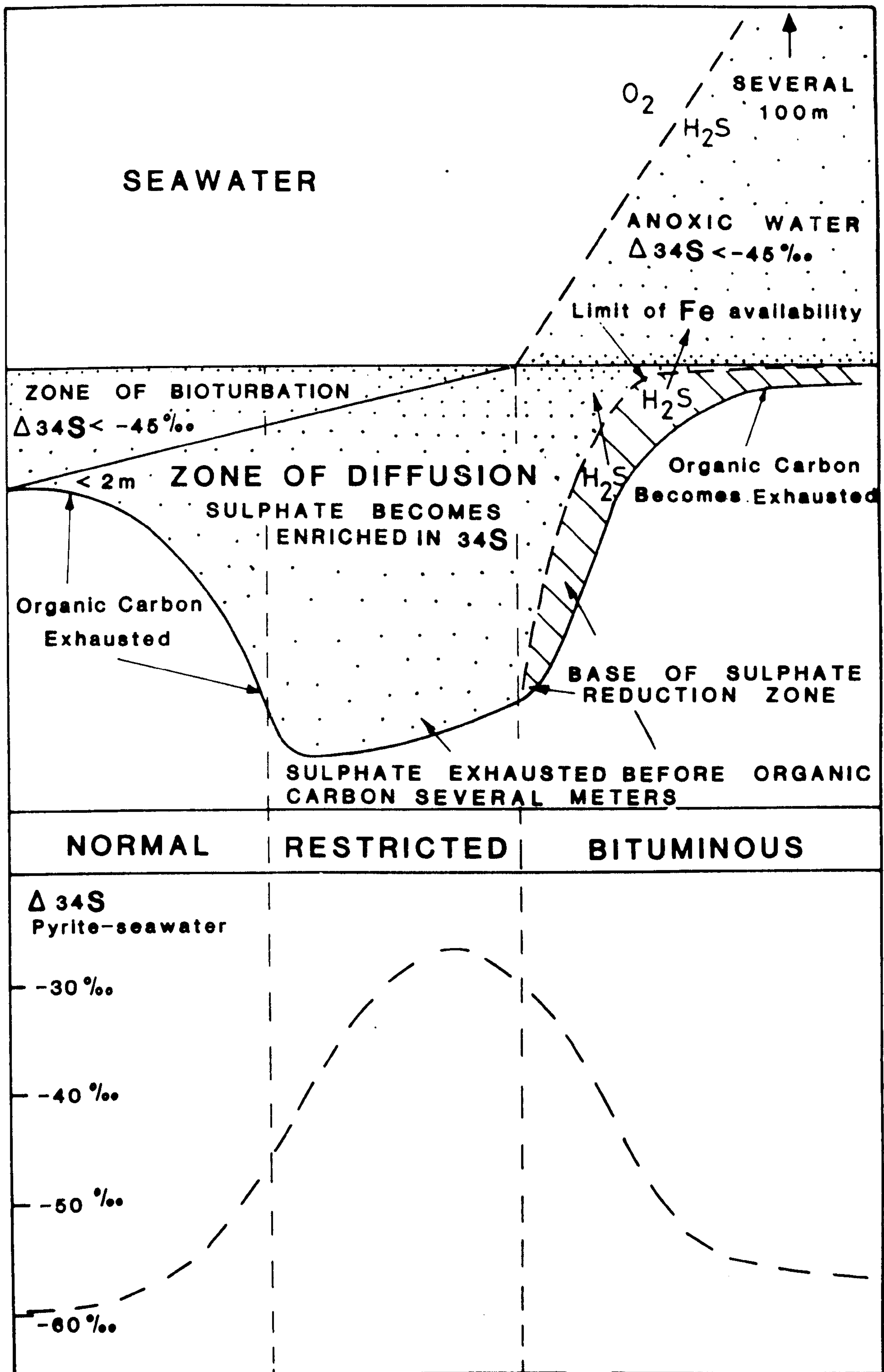


Fig 6. Environmental variations between three biofacies.  
Plot indicates controlling factors for pyrite formation  
in each biofacies.

Fig 6





Pyrite Replacement of Mollusc Shells from the Lower  
Oxford Clay (Jurassic of England)

1. Introduction.

The replacement of Mollusc shells by pyrite commonly occurs in the Lower Oxford Clay in several of the shell beds and within isolated pyrite concretions. Studies of the shells show pyritization to have occurred before during and after the crushing of the shells. The replacement of shell material by pyrite is not one of the most common forms of fossil preservation found in Jurassic Shales (See Hudson 1982) and its occurrence in the Lower Oxford Clay indicates something of the distinct early diagenetic history of that unit.

In this Chapter the pyritized shells of the three main classes of molluscs have been studied and the varying degrees of replacement of internal structure have been observed. Some shells show spectacular replacements of shell micro-structure by pyrite; others show almost total obliteration of any original internal structure. The degree of replacement of the shells and the resulting pyrite structure appear to reveal something of the method and chemistry of shell replacement by pyrite.

It has long been recognised that the Lower Oxford Clay represents a distinct preservational environment. Preservation of ammonites, gastropods, and bivalves in

their original aragonite is extremely common. This contrasts with the Upper Oxford Clay where almost all original aragonite has been dissolved (Hudson and Palframan 1969). It is of interest to note the development of pyrite within aragonitic shells and the varying effects that sulphate reduction has had on the preservation of aragonite.

Hudson and Palframan (1969) examined several different modes of fossil preservation from material mainly from the Upper Oxford Clay. Those preserved in pyrite were characteristically internal moulds with the original aragonite shell dissolved away. By way of comparison one sample of a crushed Kosmocerotid ammonite from the Basal Pyrite Shell Bed at Calvert Brick pit was examined using acetate peels and revealed pyrite faithfully replacing the nacreous structure. Duff in his thesis (1974) and monograph on the Lower Oxford Clay Bivalves (1978) remarks on the preservation of bivalve shells as pyrite replacements showing good external morphology but with no preservation of internal structure. This contrasts with the fine replacement of microstructure seen by Hudson and Palframan.

### 2. The Lower Oxford Clay.

The Lower Oxford Clay is a seemingly monotonous sequence of dark bituminous shales, which, when dry, range in colour from "Dark Olive Gray" (5Y4/1) to "Light

Olive Gray" (5Y6/1) (American Geological Institute Rock Colour Chart). The Lower Oxford Clay has been classified by Morris (1980) in his tripartite system of Jurassic mudrocks as a "Restricted shale", that is one in which the oxic/anoxic boundary lies within a few centimetres of the sediment water interface. The facies is characterized by an abundant though taxonomically impoverished benthic fauna mainly of deposit feeders tolerant of low oxygen conditions, together with ammonites. The fauna suggests that the bottom water oxygenation was poor but there is no real evidence that it ever became anoxic (Duff 1975).

The material for this study was collected from two of the London Brick Company pits, at Calvert, Buckinghamshire, and Stewartby, Bedfordshire. Fig (1) shows the stratigraphy of the two pits (after Duff 1975). The monotony of the sequence is broken at several horizons by bands of carbonate concretions; these are described by Hudson (1978); there are three at Calvert and two at Stewartby. The other noticeable features of the sections are shell beds; these probably represent accumulations of shells by increased winnowing of fine-grained material, although some of the lower oyster-rich beds show evidence for much increased current activity and may represent current accumulations (Duff 1974). It is possible that a relationship exists between the positioning of the shell beds and the concretions, as

the concretions appear to be almost always positioned within or immediately above or between shell beds.

Material was collected from three shell beds, the Basal Pyrite Shell Bed at Calvert (A on fig.1), the Mid-grossouvrei Shell Bed at Stewartby (B) and the 16' Shell Bed at Stewartby (C). Both beds A and B show discontinuous growth of concretionary pyrite which is not seen in C. These three beds belong to different biofacies under the classification of Duff (1975).

A. this is a Grammatodon shell bed and contains mainly bivalves, including Grammatodon, Palaeonucula and oysters, together with belemnites, ammonites, Procerithid gastropods and Genicularia worm tubes.

B. this is classified as a Meleagrinnella shell bed and characterized by Meleagrinnella (bivalves), ammonites, oysters and Nuculacea (bivalves).

C. This is a Nucula shell bed and contains mainly the bivalves Nuculacea and Meleagrinnella with Procerithium and Dicroloma (Gastropods).

As well as the material from the shell beds several pyrite concretions were examined. These represent the growth of pyrite around crushed macroconch ammonites. Concretions of this kind are found throughout the sequence and do not appear to be abundant at any particular horizon. The particular samples examined were collected loose in the pit. Comparable material found in situ tended to be weathered and unsuitable for



sectioning.

### 3. Preparation of samples.

The ammonite concretions and samples from beds A and B which contained concretionary pyrite were examined as polished sections with reflected light. Samples from bed C where the clay was not cemented by pyrite were separated as isolated shells, and treated with 10% acetic acid to remove the remaining carbonate, mounted on double sided sticky tape and coated with gold for examination by Scanning Electron Microscopy.

### 4. General Description of samples.

#### 4.1 Ammonite concretions.

Three ammonite concretions were collected from Calvert (C1, C2 and C3), these are in the form of pyritic discs about 150mm in diameter. C2 and C3 are distinctly knobbly in appearance and contain other pyritized fossils including Nuculid bivalves, Genicularia, and procerithid gastropods. C1 is smoother in appearance and is significantly thinner than the the other two (about 1cm as compared to a least 2cm for C2 and C3). When sliced C2 and C3 showed the remains of crushed Kosmoceratid ammonites, which when cut at the right angle still show nacreous lustre (Fig 2b,c,d). The degree of replacement of shell material by pyrite can be



seen to vary. Some areas showing pink aragonite while others appear to be completely replaced by pyrite. When C1 was sliced no shell material, original or replaced was found. From its outward appearance there was no doubt that the concretion had formed around an ammonite, albeit crushed. It proved necessary to examine polished sections to find any remains of shell material. The matrix pyrite of the concretions is finely crystalline and cut by networks of approximately 1mm thick veins; some are lined with pyrite, though most are filled with calcite.

A further ammonite concretion was collected from Stewartby (S1): this sample was broken probably by pit working. This ammonite appeared less crushed than the samples from Calvert and more of the external ribbing of the shell could be seen, although these were inflated by the growth of pyrite on the outside of the shell. The interior of the ammonite was completely filled with fine-grained pyrite.

### 4.2 Shell bed material

Samples from the Basal Pyrite Shell Bed (A) show clusters of shells in a concretionary matrix of pyrite. The concretionary pyrite is more granular in texture than that seen in the ammonites and euhedral crystal faces can be seen in hand specimen with a lens. The fossils show coatings and replacements of pyrite with

euohedral pyrite filling the cavities. Some shells show geopetal infillings with pyrite in the bottom and later sparry calcite on top. Several shells show sparry calcite filling the voids and in some cases where the shell has been dissolved forming casts (Fig 3).

In the Mid-grossouvrei shell bed (B) the pyrite matrix around the shells is much finer in texture than that of bed A and resembles more that of the ammonite concretions. Euhedral crystals can be seen filling shell cavities but sparry calcite is not present in this bed.

Samples of pyritized Nucula were separated from the 16' Pyrite Shell Bed (C). These show good external morphology with little compaction; sometimes there are a few fractures along the ventral margin. Some show the formation of a few euohedral pyrite crystals within the shell, but no other formation of pyrite infillings or concretionary pyrite matrix is seen in this bed.

### 5. Concretionary Pyrite in Polished Section.

#### 5.1. Shell beds.

The concretionary pyrite of the Mid-grossouvrei shell bed is of the "Aggregated" form, as described by Hudson (1982) (Fig 5c right hand side). This consists of aggregates of finely crystalline pyrite about 10 to 20  $\mu\text{m}$  in diameter. The shell infillings (Fig 5c left hand side) are of equant pyrite of about 10 to 50  $\mu\text{m}$ . In the

Basal Pyrite Shell Bed both the external pyrite matrix and the shell infillings are of equant pyrite (fig 5d).

### 5.2. Ammonite concretions.

The pyrite matrix of samples C1,2 and 3 is of the same aggregated pyrite texture as is seen in the Mid-grossouvrei shell bed (Fig 5a & b), although they tend more to the small 10µm size. The pyrite crystals lining the cracks in the matrix are equant in form mainly octahedra and cubes with octahedral faces (Fig 4b) . A bladed habit (Fig 4a) is seen lining the cracks in sample C3. Hudson (1982) described pyrite of this habit from the Lias6; although the crystals he figured were smaller and tended to be finer they corresponded in general shape to those seen in C3.

## 6. Pyrite Texture in Replaced Kosmoceratid Shells from Ammonite Concretions.

Three distinct textures can be seen in the the heavily pyrite-encrusted ammonites.

1. A texture resulting from the original structure of the shell, resulting from the replacement of the organic matrix by pyrite.
2. An ovoid texture seen in several stages of replacement.
3. Euhedral crystals lining cracks and growing into the

shell.

### 6.1 Replacement of Organic Matrix of The Shell.

This texture is found in sample C3, where the organic matrix around the nacre bricks is replaced by pyrite leaving the aragonitic shell (Fig 6a). The overall appearance is dependent on the original structure of the shell, which has not been significantly modified by the growth of pyrite.

### 6.2 The Ovoid Pyrite Replacement Texture.

This is a ubiquitous texture seen at several stages of replacement. The ovoid structures range in size from 5 to 10 $\mu$ m upto 100 to 200  $\mu$ m, averaging about 20-30 $\mu$ m. These ovoids occur as single isolated structures in otherwise unreplaced shell through to later stages where the shell is replaced by coalescing ovoids. Fig (6b,c &d,) shows a range of occurrences of this texture. In Fig 6b (Sample C3) an early form of the ovoid texture is seen as slightly diffuse aggregates within a portion of shell where pyrite has partially replaced the organic matrix. In Fig 6c (Sample C2) ovoid structures are seen at two stages of replacement. In both stages they show a common feature, concentric brighter and duller banding. The dull areas show up bright when the polars are crossed; this is due to the internal reflections of carbonate inclusions within the pyrite. Some of the

later brighter structures show flatter sides and angular termination; this suggests that some of the later growths are single crystals. The earlier replacements are duller and show more conspicuous banding than the later. The long axes of these ovoid structure can be seen to lie along the grain of the shell. In Fig. 6e (Sample S1) the left hand side of the photograph shows the replacement being made up of coalescing ovoids. The right hand side of the photograph shows large ovoid structures with conspicuous banding. Both the larger and smaller ovoids appear to be replacing an earlier phase in the centre of the picture. Under crossed polars this area shows low bireflectance and crystals with arrowhead terminations; both these characteristics are indicative of marcasite.

### 6.3. Euhedral Crystals along Cracks and Fractures.

These are seen lining the late cracks and fracture in the shells. Euhedral crystals are seen to have grown both inwards and outward from the margin of the crack. Some of the cracks are seen to be continuous with those in the matrix pyrite. In Fig 6f (C2) the crack lining is seen to coalesce with a subspherical texture. In Fig 6g (C2) pyrite halos are seen around the edges of shell fragments.



7 Phases of Replacement in Ammonite Concretions.

The replacement of the ammonite shell material by pyrite can be seen to fall into two phases. These are recognised predominantly by the brightness of the pyrite which is dependent on the amount of carbonate material remaining.

7.1 Phase 1 is noted by areas of dull replacement pyrite with large amounts of relict carbonate, this is revealed by its strong internal reflectance under crossed polars. Fig 7c & d show this very well with dull pyrite showing under plain polarized light and the bright patches of carbonate when the polars are crossed. It appears to be the carbonate that gives the shell its nacreous lustre in polished blocks.

Phase 1 can be divided into three stages representing the degree to which the original carbonate is present. Stage 1A represents the replacement of the organic matrix with no solution of the aragonite bricks. Stage 1B the early growth of diffuse ovoid aggregates. Stage 1c is the replacement of large areas of shell by dull pyrite due to the coalescence of large numbers of ovoid pyrite structures. The differences between stages 1A and 1B may not lie in the timing of replacement but in original structure of the shell. The initial stage 1B ovoids probably results from pyrite growth at organic

concentrations in the shell. The formation of the marcasite in sample S1 probably occurred during phase 1 prior to the crushing of the shell and the formation of the phase 2 replacements that cut across it. The formation of marcasite is probably due to unusual chemical conditions in that part of the shell possibly a lower pH, as the formation of marcasite is thought to be promoted by lower pHs.

7.2 Phase 2 is characterized by the bright carbonate inclusion free pyrite. The phase appears to be associated with cracking and fracturing of the shell, possibly leading to the freer access of iron and sulphate into the shell. phase 2 replacements can be seen concentrating along and spreading out from such cracks and lines of weakness parallel to the margin of the shell, which have opened up during the crushing. This is shown in Fig 7c (top left corner) where bright ovoids are seen between two cracks in the shell. Figs 7a&b show a concentration of bright phase 2 pyrite along a line running parallel to the shell margin and decreasing to isolated spheres in the stage 1c pyrite towards the bottom of the photograph. The ovoid pyrite of phase 2 can be seen to be contemporaneous with the pyrite lining the cracks and fractures. In fig 6f the bright phase 2 ovoids can be seen to merge into the euhedral crack lining.

The bright phase 2 ovoids appear, in some photographs, to be replacements of pre-existing phase 1 ovoids, eg. those in fig 6 c&f, where the bright ovoids are more densely replaced phase 1 ovoids. In certain cases though, phase 2 ovoids can be seen cutting the pre-existing phase 1 (Fig 7a), indicating that the ovoid texture was initiated in both phases. The occurrence of the large phase 2 ovoid texture in S1 replacing the marcasite, which shows no ovoid texture, indicates that the ovoid texture in phase 2 is a result of the mode of replacement occurring at that phase and not a relic of any earlier texture. In C2 the phase 2 ovoids were seen with the nacreous shell banding passing through it. This appears to indicate that at that point the shell underwent a stage 1A replacement prior to the phase 2 ovoid formation.

### 8. Shell Replacement in Gastropods and Bivalves from Shell Beds.

The smaller Procerithid gastropods and Nuculid bivalves often show more faithful replacement of original shell structure by pyrite, than do the larger Kosmoceratid ammonites. Many of the smaller shells have resisted crushing far better than the ammonites. The Procerithid gastropods often show better replaced microstructure than the Nuculids, though both show a

range of replacements.

Four distinct types of replacement are seen in the material from the three shell beds.

1. Replacement of organic shell matrix by pyrite showing good microstructure. This is seen especially in the gastropods.
2. Replacement showing outwardly good preservation of morphological features, but internally only the gross structure such as growth lines is preserved. This is often seen in the Mid-grossouvrei Shell Bed and the 16' Shell Bed.
3. Replacement of shells by the euhedral concretionary pyrite leaving only lines of carbonate inclusions at the margins of the shell. This is most notable in the Basal Pyrite Shell Bed.
4. Replacement of the central parts of the shell with aggregated pyrite often separated from the shell by a band of bright euhedral pyrite.

In type 1 replacement the organic matrix of the shell is replaced leaving the the carbonate more or less unaffected Figs 8a,b&c. In fig 8a the shell is viewed under crossed polars and and shows differential extinction of carbonate due to its original arrangement in the shell. Several shells showing this type 1 replacement have the central portions replaced by later aggregated and euhedral pyrite (Fig 8b) or, in the Basal



Pyrite Shell Bed, by sparry calcite (Fig 8a).

In type 2 replacement the replacement occurs preferentially along the outer margin and growth lines of the shell. Some show a thin band of well preserved microstructure along the outer margin of the shell with successive bands of replacement in the central parts of the shell which have dissolved and obliterated the original carbonate structure. In some cases the replacement is incomplete and aragonite remains in the core of the shell (Fig 9b & 10). The S.E.M. photographs (Fig 9c&d) shows the inside surface of such a shell with the aragonite dissolved away. The euhedral nature of the replacement pyrite (cubes with modified octahedral faces) is clearly seen. The bands of crystals appear to correspond to the preferential replacement along growth lines. The successive bands of replacement seen in fig (9a) appear to result from the introduction of pyritizing solutions through cracks in the shell.

The type 3 preservation is seen in fig 8e of the Basal Pyrite Shell Bed. The two lines of inclusions correspond to the outer and inner margin of the shell. The pyrite crystals are more tightly packed at the shell margin than in the general matrix and can be seen in fig 8d to grow undisturbed across it.

Type 4 replacement in the central parts of the gastropod shells seen in Fig 8b results from the opening of cracks in the shell and appears to be continuous with



the external aggregated pyrite. In the Basal Pyrite Shell Bed the central parts of the shell are replaced with sparry calcite.

#### 9. Relationships Between Pyrite Replacements in Shell Beds.

The difference between the gastropods, showing good microstructure, and the bivalves, which show poor preservation of microstructure, probably represents some intrinsic difference in the construction of the two kinds of shell. The significant difference may be the thickness of the shell. The thinner Procerithium shells allowing freer access of solutions into the centre of the shell. The thicker Nuculid shells only allow the solutions into the outer parts of the shell and along the growth lines. The replacement of the shells in the Mid-grossouvrei Shell Bed occurs prior to the formation of the aggregated concretionary pyrite and the infilling euhedral pyrite, as the continuations of the two types of pyrite can be seen replacing the central parts of the shell. The replacement of shell in a similar manner to the Mid-grossouvrei Shell Bed also occurs in beds where the concretionary pyrites have not formed, eg. the 16'Pyrite Shell Bed.

The principal mechanism of replacement in the Basal Pyrite Shell Bed is distinctly different from that found

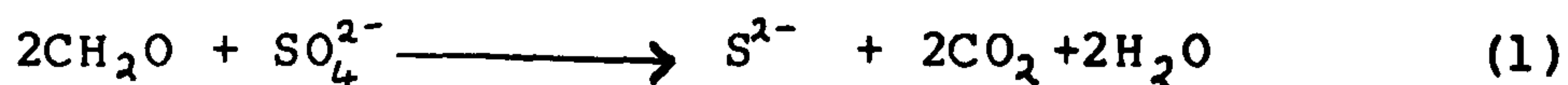
in the other beds studied. Few shells show any microstructure and most show type 3 replacements. Other features distinguish the Basal Pyrite Shell Bed; the lack of aggregated pyrite and the replacement of the central parts of shells by sparry calcite.

Hudson (1982) suggested that aggregated pyrite may form due to pyrite growth in a mud or organic-rich matrix, whereas the euhedral pyrite probably represents growth in a void. This explains the occurrence of aggregated pyrite outside and euhedral pyrite inside the shells of the Mid-grossouvrei Shell Bed. This seems to indicate that the Basal Pyrite Shell Bed was deposited with little or no mud. The lack of mud may also explain the other differences, ie. the open structure of the bed allowed freer movement of solutions enabling the formation of the sparry calcite and also caused a shift in the position and thickness of the sulphate reduction zone, which resulted in the different pyrite textures.

### 10. Chemistry of Shell Replacement by Pyrite

The formation of pyrite in the shell structure of molluscs occurs by the bacterial reduction of seawater sulphate. Hudson and Palframan (1969) demonstrated that the organically-bound sulphur was insufficient to account for the mass of pyrite formed. The bacterial reduction of sulphate can be expressed by the following

equation(1),



This equation is unrealistic as S and CO are not normally coexisting species. The organic matter, expressed in the equation as a simple carbohydrate, is probably initially supplied by the organic matrix of the shell, but, as nacreous contains only about 1% organic C and cross lamellar shells less (Hudson 1967), other sources of organic matter must be introduced to explain the extensive replacements of the shells. Sulphate and iron, for the conversion of sulphide to pyrite, are supplied by diffusion from outside the shell. Coleman and Raiswell (in press) have demonstrated that a balance exists between the precipitation of pyrite and carbonate depending on the availability of iron. If iron is limited during the reduction of sulphate then S may become hydrolyzed liberating hydroxyl ions which can lead to the precipitation of carbonate if H S or HS species are allowed to diffuse out of the system (EQ 2,3 and 4).



If iron is present the equation may be rewritten (EQ 5).



The potential  $\text{H}^+$  ions lead to a shift in the carbonate equilibria, allowing the solution of carbonate (EQ 6).



Therefore by varying the availability of iron it is possible to alter the extent of precipitation and solution of carbonate. The formation of pyrite in the shell is dependent on the entry of sulphate and iron into the shell. In the earlier stages of replacement this is achieved by diffusion utilizing the natural porosity of the shell, hence the thinner gastropod shells yield better preservation than the Nuculids. At early stages of replacement the retention of good microstructure relies on the lack of solution of carbonate. This would suggest that initially insufficient iron was present to satisfy the sulphide produced. One possibility for a limitation of iron may be that the surrounding sediment was not totally anoxic. As iron is only free to diffuse when it is in the ferrous form it is necessary for conditions to be reducing. The shell may have initially constituted a micro-reducing environment in the sediment possibly due



to the organic-rich nature of the dead animal. The external Eh conditions of the sediment may also explain the differences in preservation between the Basal Pyrite Shell Bed and the other shell beds. If the Basal Pyrite Shell Bed was deposited clean of mud, the circulation of aerobic water would have been promoted. The oxic nature of the sediment did not allow the reducing micro-environments to form in the shells and the early type 1 and type 2 replacement did not occur. When the sediment finally became anoxic, the free availability of iron and sulphate and the organic matter of the shell allowed sulphate reduction to commence at the outside of the shell, with pyrite crystals growing inwards dissolving the shell and, due to the lack of mud, outwards into the void. In the Mid-grossouvrei Shell Bed the muddy nature of the sediment allowed the sediment to become depleted in dissolved oxygen sooner, and anaerobic micro-environments to form within the shell, leading to the early faithful replacement of the shells to occur.

The ovoid texture found in the ammonite shells appears to suggest the effects of diffusion, especially when the banding is present. The ovoids probably form around distinct centres of reduction, possibly initially more organic-rich sites. Sulphate diffuses in and is reduced; this then diffuses out against the inward gradient of iron. If the diffusion gradients are



balanced then the precipitation of iron sulphides will occur as discrete bands around the centre, in an analogous manner to iron oxide bands in Liesegang weathering. In the later stages of reduction the number of centres increases, possibly reflecting an increased supply of sulphate, giving rise to the more densely packed coalescing replacements. Solution of carbonate is more widespread at the later stages and the banding often less pronounced, this may well be due to an increased supply of iron. At later stages the in situ organic supply will become exhausted, and for the continuation of reduction it is necessary to postulate that soluble organic matter was also supplied to the sites of sulphate reduction in the shell.

It is worth noting that a link may exist between the solution of shells and the formation of the carbonate concretions described by Hudson (1978). Apart from one all concretion horizons in the Lower Oxford Clay occur within or immediately above or between shell beds. Hudson found that the pore water carbonate from which the concretions formed evolved from an early negative  $\delta^{13}\text{C}$  value (-15 to -20) towards more positive values. If we consider the isotopic composition of the carbonate resulting from the sulphate reduction and the solution of the shells. In the early stages the replacement of shells occurs with little shell solution and the resulting carbonate in solution will be

dominated by sulphate reduction carbonate derived from the organic matter at -25‰ with a little primary shell carbonate at 0‰. This would yield the early -15 to 20‰ values of the concretions. As the replacement of the shells continues a larger proportion of shell materials dissolved, causing the dissolved carbonate to become more positive, which is the trend seen in the concretions. It is therefore pleasing to speculate that the pyritization of shells in the shell beds promoted the formation of the concretions.

#### 11. Timing of Replacements.

The formation of pyrite is not limited to totally anoxic environments (Hudson and Palfreman, 1969). Pyrite may form within local anoxic micro-environments as suggested above. Such micro-environments may form around and within shells dead or living. Clark and Lutz (1980) described pyrite replacement of recent living bivalves. It is not proposed that all the early replacements seen in the Lower Oxford Clay commenced while the animals were still alive, although it is a possibility for the infaunal Nuculids. The results of Clark and Lutz indicate that shell replacement may occur very early in the diagenetic history of the sediment. The later stages of replacement almost certainly occurred when the sediment was totally anoxic and had

undergone sufficient burial to crush the large macro-conch ammonites. Sulphur isotope analyses from the ammonite concretions show significant enrichment in  $^{34}\text{S}$  upto 40‰ (Chapter 3) compared to Jurassic seawater at +16‰, a process which occurs with depth due to preferential removal of  $^{32}\text{S}$  by bacterial sulphate reduction. The exact depth of crushing of shells is not known and almost certainly varies from one shell to the next. The large macro-conch ammonites are probably more susceptible to crushing than the smaller gastropods and Nuculids. The early pyrite replacement of the shell may have helped to reduce the effects of crushing. The ammonite concretion C1 in which the ammonite has undergone no early replacement has suffered from more extensive flattening than the other concretions. The lack of mud in the Basal Pyrite Shell Bed resulted in the delaying of the onset of pyritization, which resulted in the distinct preservational types found in that bed.

## 12. Conclusions.

Pyrite replacement of shells in the Lower Oxford Clay results from the bacterial reduction of sulphate occurring within the shell, the bacteria initially making use of the organic matrix of the shell as a substrate. The replacement show varying degrees of



carbonate solution which is thought to relate to the availability of iron at various stages of replacement. Early replacement of the shell probably occurred in the top oxic layer of the sediment, with the shell constituting a reducing micro-environment. Sulphate and iron were supplied to the shell by diffusion and the ovoid texture found in ammonite probably results from diffusion occurring at discrete centres of reduction in the shell. On further burial the sediments became more reducing and iron became more freely available leading to greater solution of the aragonite shells. The crushing of the shells allowed the freer access of iron and sulphate and, by that stage, soluble organic matter, which lead to more extensive replacement of the shells at the exspense of the original shell structure. Early pyritization helped some shells to resist crushing and these retain more of the earlier replacement structures. The lack of sediment in the Basal Pyrite Shell Bed delayed the onset of reducing conditions, and the resulting preservations do not commonly show the early faithful replacements. The pyrite replacement of shells may have yielded some of the carbonate for the concretions within the Lower Oxford Clay. The study of the replacement of mollusc shells shows us how the preservation of fossils may help us elucidate something of the environment of deposition and the early diagenetic history of sediments.

List of Figures

All measurements in millimetres unless otherwise stated.

Fig 1      Sections of Stewartby and Calvert Brick pits  
              (After Duff 1975) from which samples of  
              pyritized shell were derived. Bed A =Basal  
              Pyrite Shell Bed. Bed B= Mid-grossouvrei Shell  
              Bed. Bed C= 16' Shell Bed.

Key to Biofacies.

1. Silts and silty clays
2. Blocky claystone
3. Calcareous clays
4. Meliagrinnella shell bed
5. Nucula shell bed
6. Grammatodon shell bed
7. Deposit feeder bituminous shales
8. Grammatodon-rich bituminous shales
9. Foram-rich bituminous shales
10. Gryphea shell bed

Fig 2      Sliced ammonite concretions  
              2a sample C1 showing no replaced shell  
              2c sample C3 showing irregular outline due to  
              inclusion of Nuculids etc in the concretion.  
              2b & d sample C2 showing nacreous lustre of  
              replaced shell material

Fig 3      Sketches of shells



3a Gastropod shells from the Basal Pyrite Shell Bed showing geopetal infillings of calcite and pyrite

3b Nuculid from the 16' Shell Band show replacement of shell along growth lines and relict aragonite shell in the centre.

3c Gastropod from the Basal Pyrite Shell Bed shows small amount of pyrite infilling with later solution of shell and formation of a calcite cast.

Fig 4 Pyrite lining cracks in ammonite concretions

4a sample C3 showing bladed pyrite

4b sample C2 showing euhedral pyrite

Fig 5 Types of concretionary and matrix pyrites from ammonite concretions and shell beds

5a Sample C2 showing aggregated concretionary pyrite

5b Sample C1 showing aggregated concretionary pyrite.

5c Mid-grossouvrei Shell Bed showing aggregated pyrite outside and euhedral pyrite inside a gastropod shell

5d Basal Pyrite Shell Bed showing euhedral pyrite inside and outside shells

Fig 6 Pyrite replacements of ammonite shells

6a Pyrite replacing organic matrix between nacre blocks from sample C3

6b Early ovoid texture developing in partially replaced shell of C3

6c C2 showing 2 phases of ovoid texture, early dull ones showing conspicuous banding and late bright ones with less conspicuous banding

6d Portion of C2 showing 2 phase of replacement by coalescing pyrite ovoids. Earlier phase dull later bright

6e S1 showing late stage replacement of shell by small coalescing ovoids (Left), by large ovoids (right). The centre appears to be replaced by an earlier phase of marcasite

6f Crack lining merging with late ovoids (C2)

6g Carbonate shell surrounded by pyrite halos (C2)

Fig 7 Sample C2 showing 2 phases of replacement in normal and crossed polars. Early phases show relict carbonate under crossed polars not present in the later phases of replacement.

Fig 8 Replacements of gastropods from shell beds.

8A Replaced gastropod from the Basal Pyrite Shell Bed showing stripy appearance under crossed polars due to the extinction of relict shell carbonate.

8B Replaced gastropod from the Mid-grossouvrei Shell Bed showing pseudo-prismatic shell structure replaced by

pyrite and the central parts of the shell replace by aggregated pyrite through cracks in the shell

8C Replacement of gastropod from the Mid-grossouvrei Shell Bed showing both pseudo-prismatic and cross lammellae shell structure.

8D & 8E Replacement of gastropod shell from the Basal Pyrite Shell Bed leaving lines of carbonate inclusion along the inner and outer margins of the shell. 8E shows a close up of the pyrite crystals growing across the margin of the shell.

Fig 9 Replaced bivalves from shell beds.

9A & B Replaced Nuculid bivalves from the Mid-grossouvrei Shell Bed. 9A show concentric replacement of central parts of the shell. 9B shows preferential replacement around the edge of the shell and along growth lines.

9c & D Scanning electron microscope photographs of the inside surfaces of replace Nuculid shells from the 16' shell bed with relict aragonite dissolved away. 9D shows close up of the euhedral crystals mainly cubes with modified octahedral faces. Bands of larger crystals in 9C probably represent preferential replacement along growth lines.

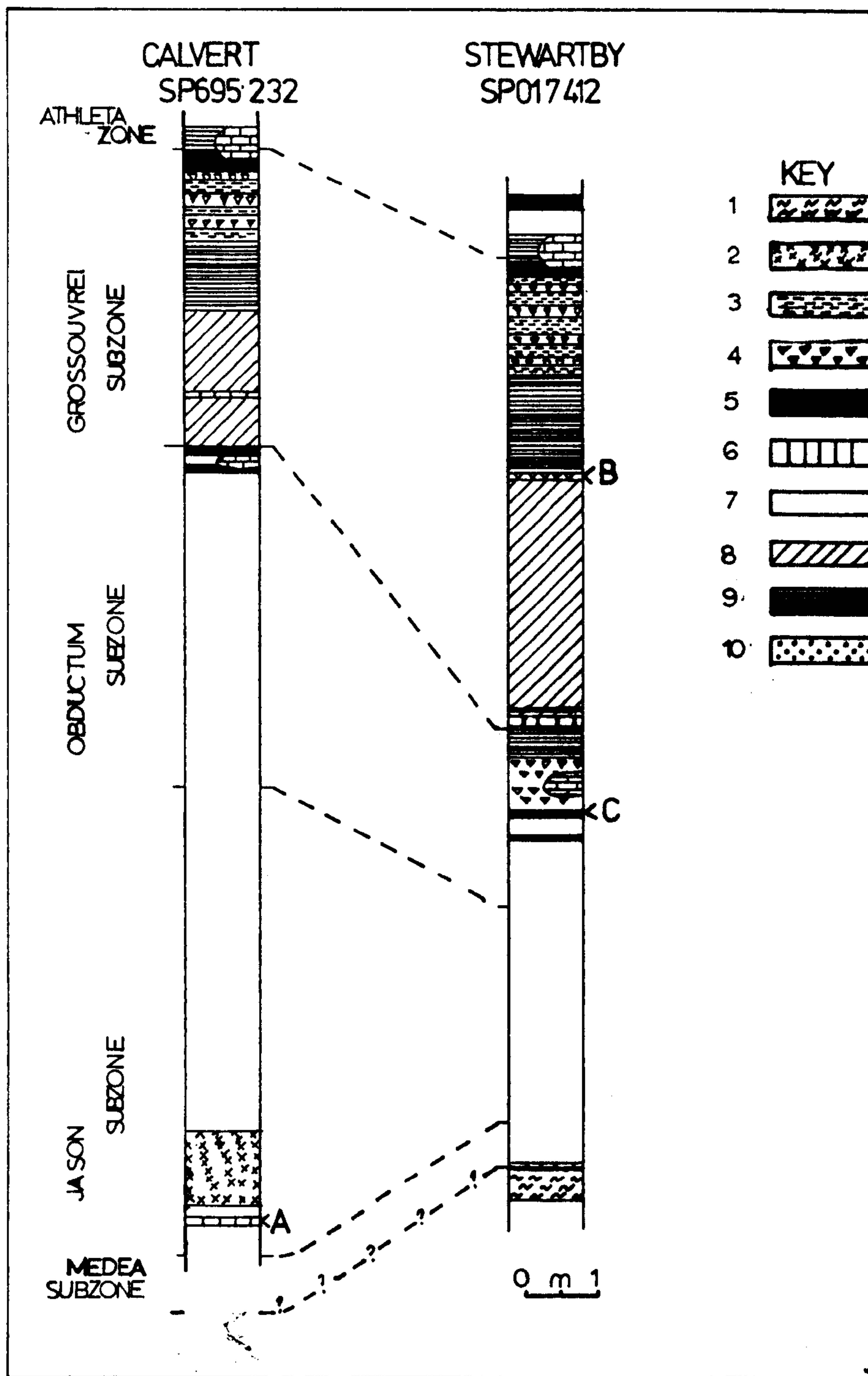
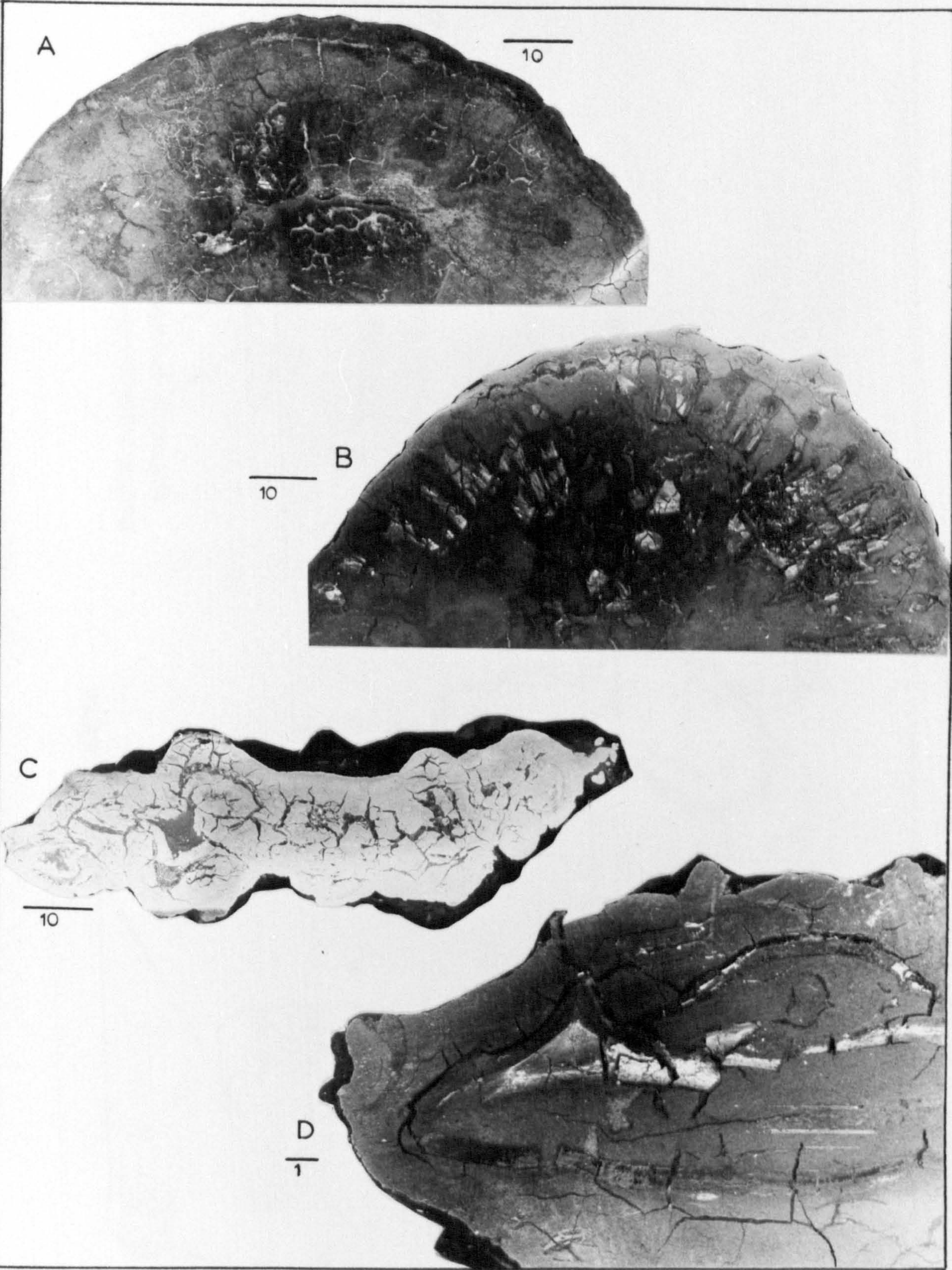




FIGURE 2



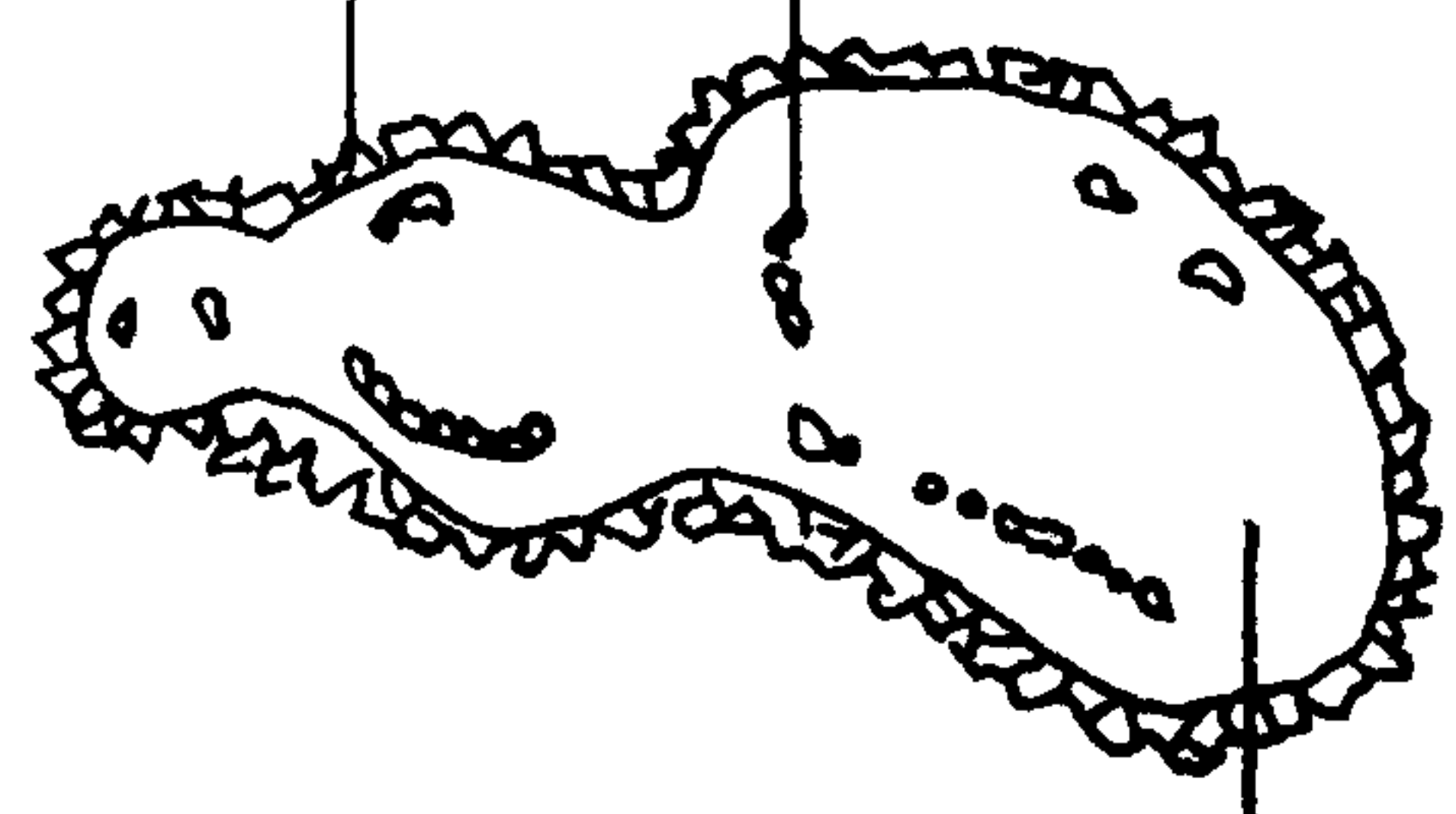


sparry calcite



A  
2mm

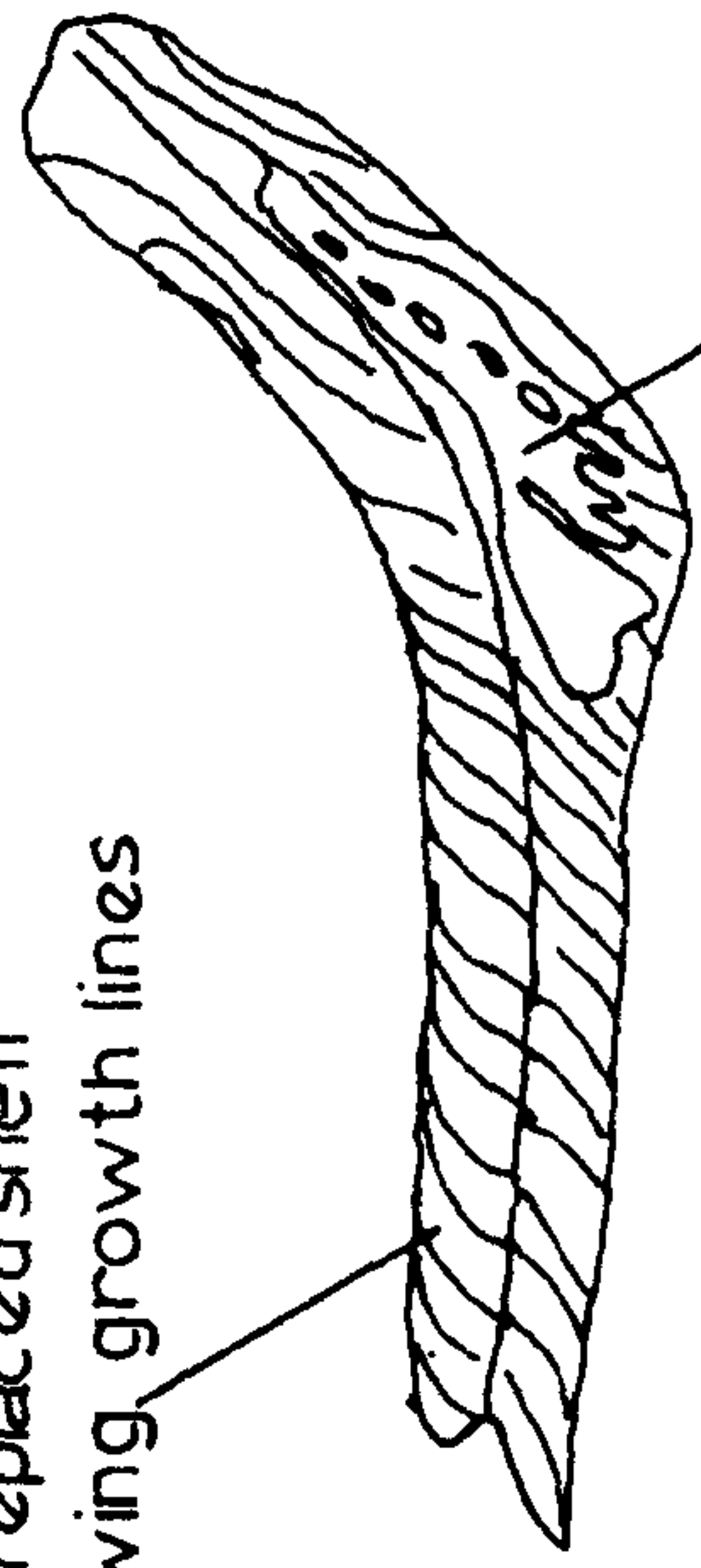
euhedral pyrite



sparry calcite

C  
5mm

pyrite replaced shell  
showing growth lines



B  
5mm

relict aragonite

euhedral  
concretionary  
pyrite

euhedral pyrite  
infilling



FIGURE 5

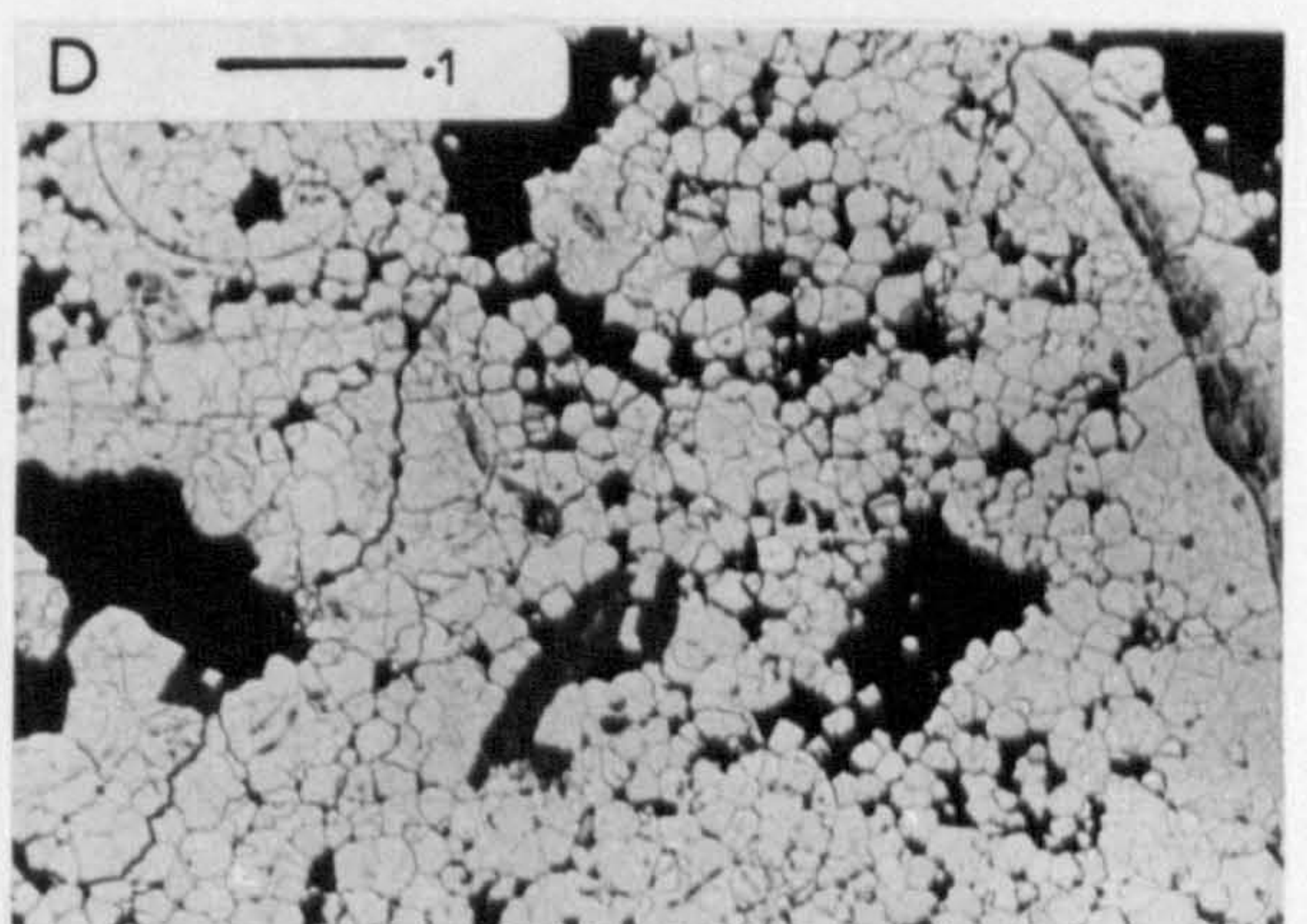
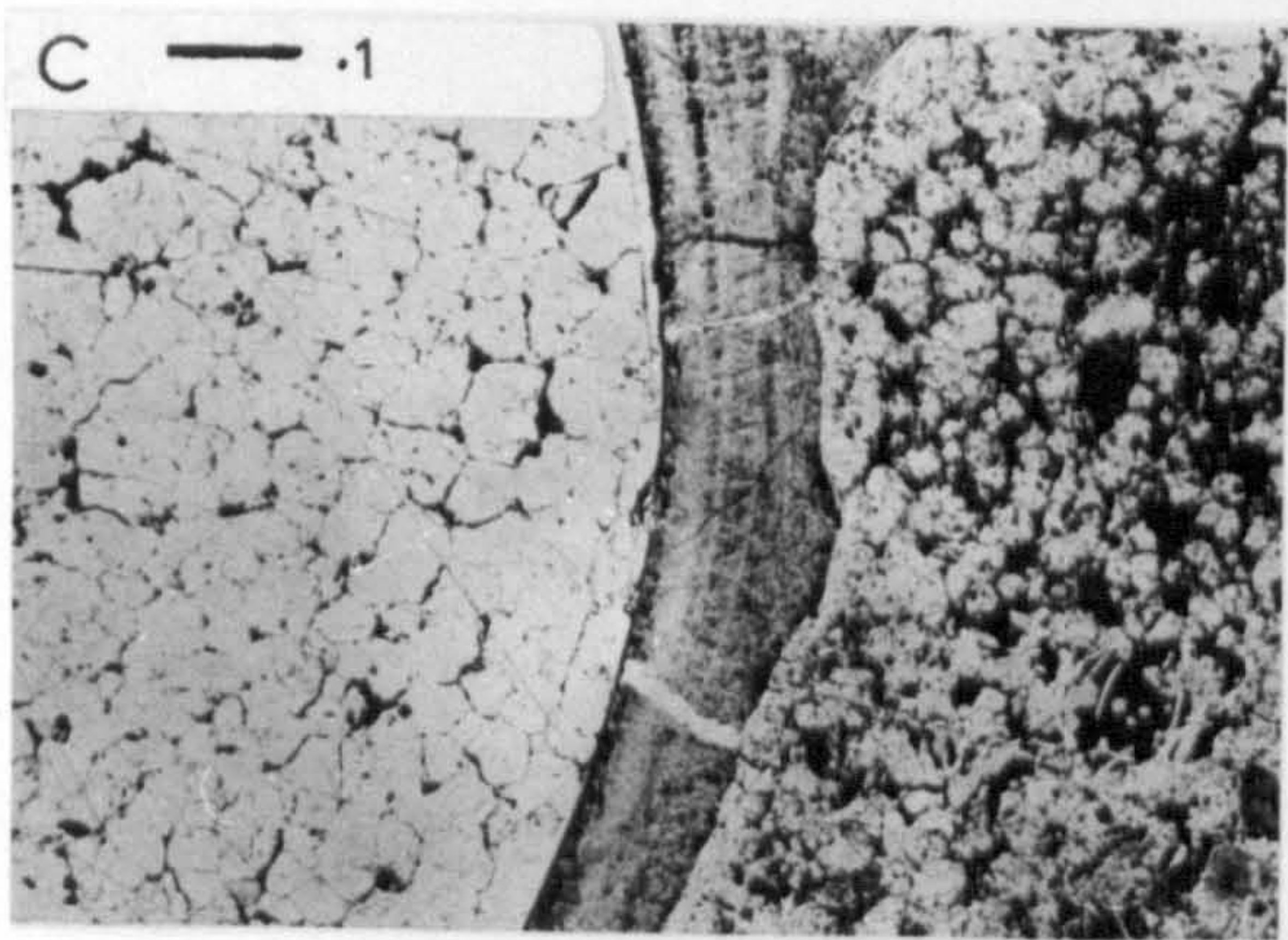
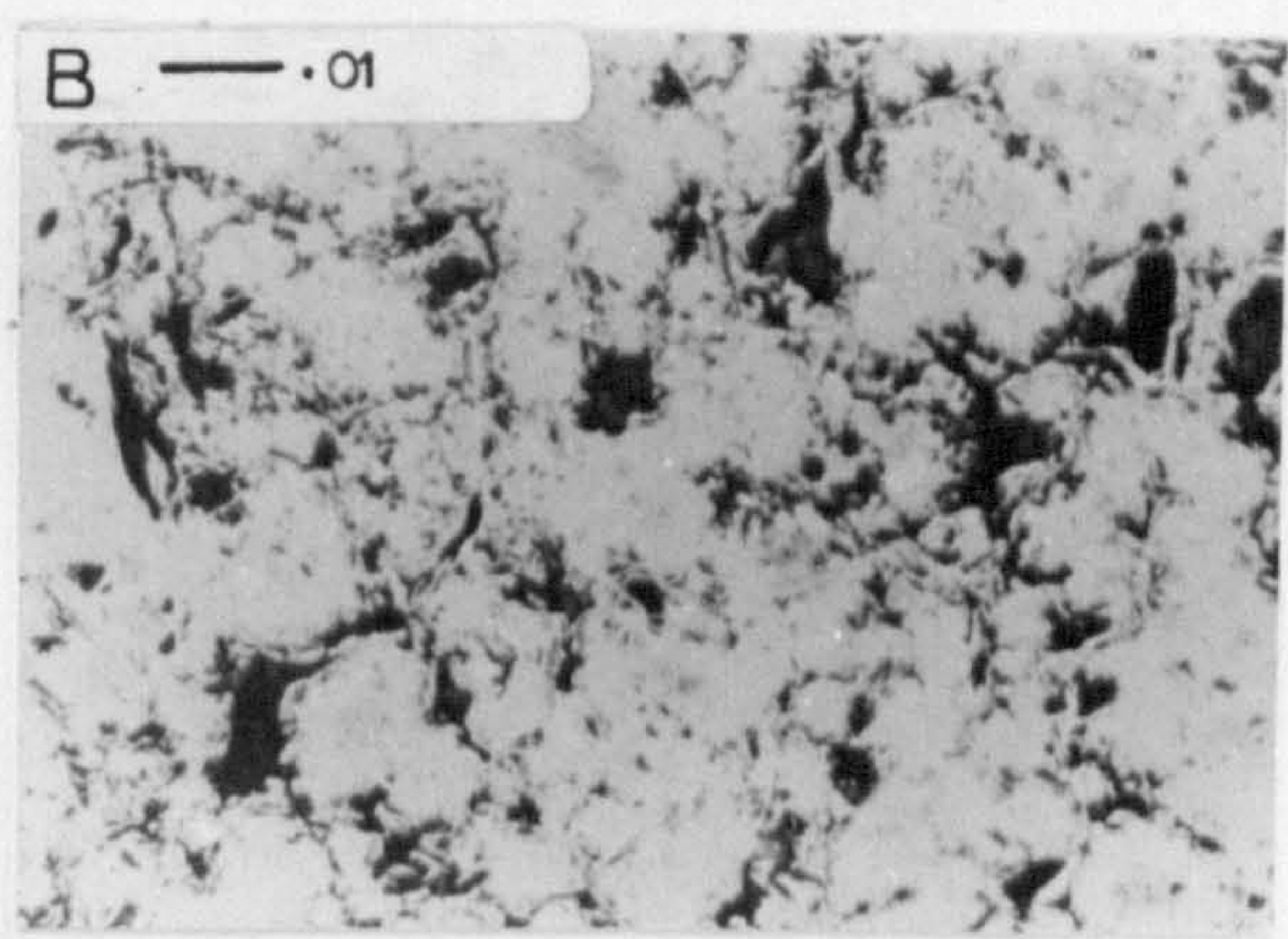
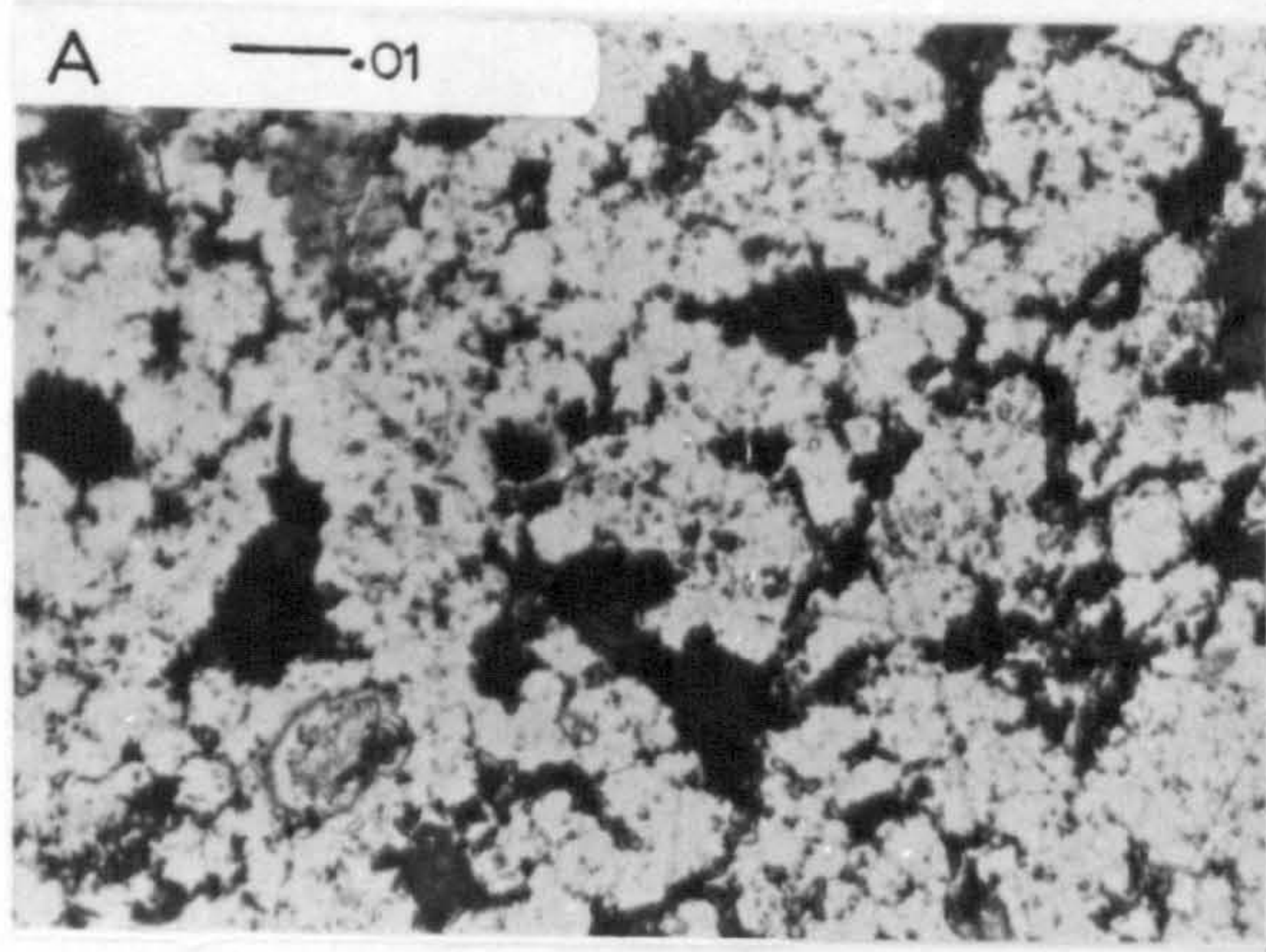


FIGURE 4

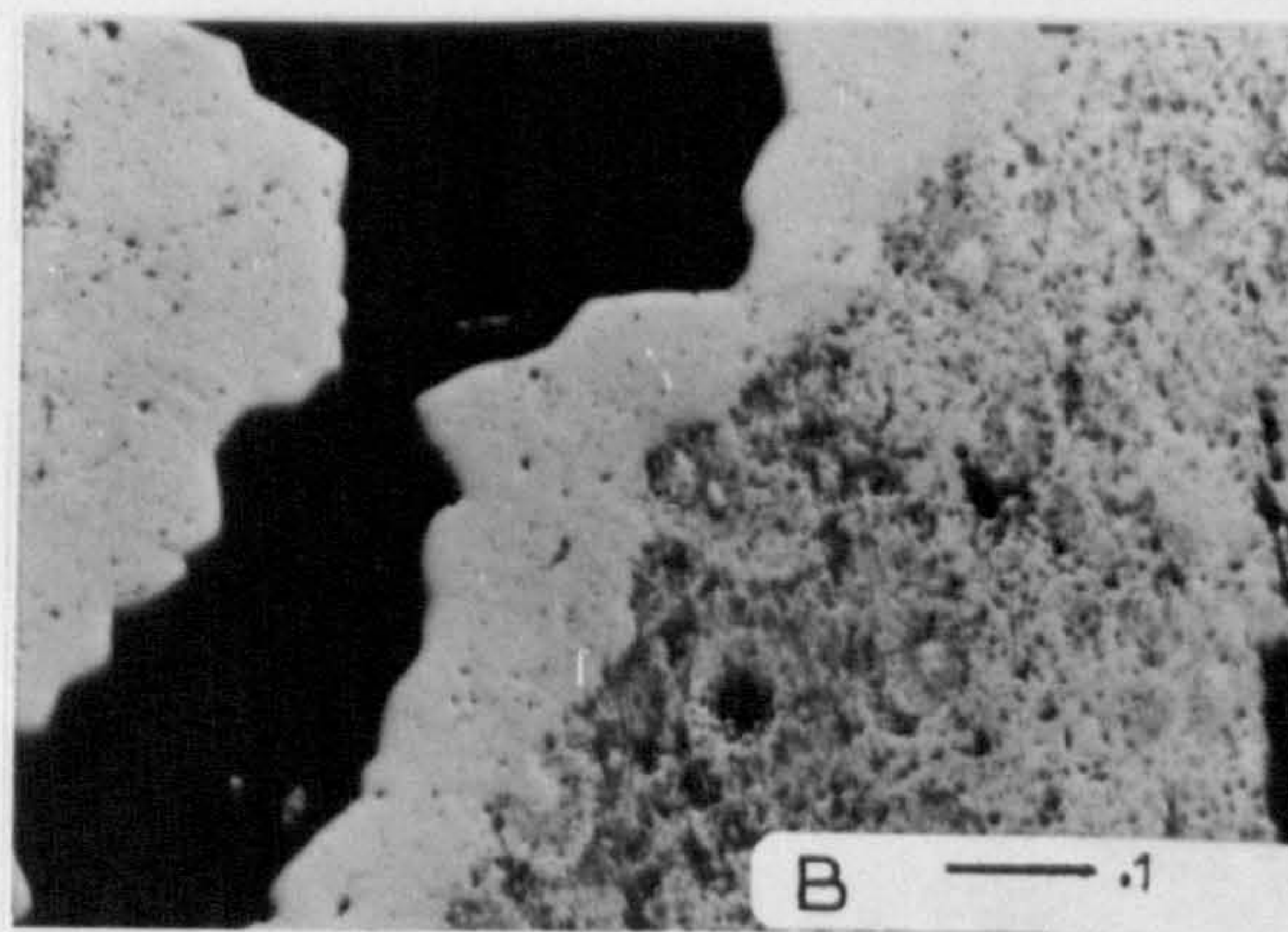
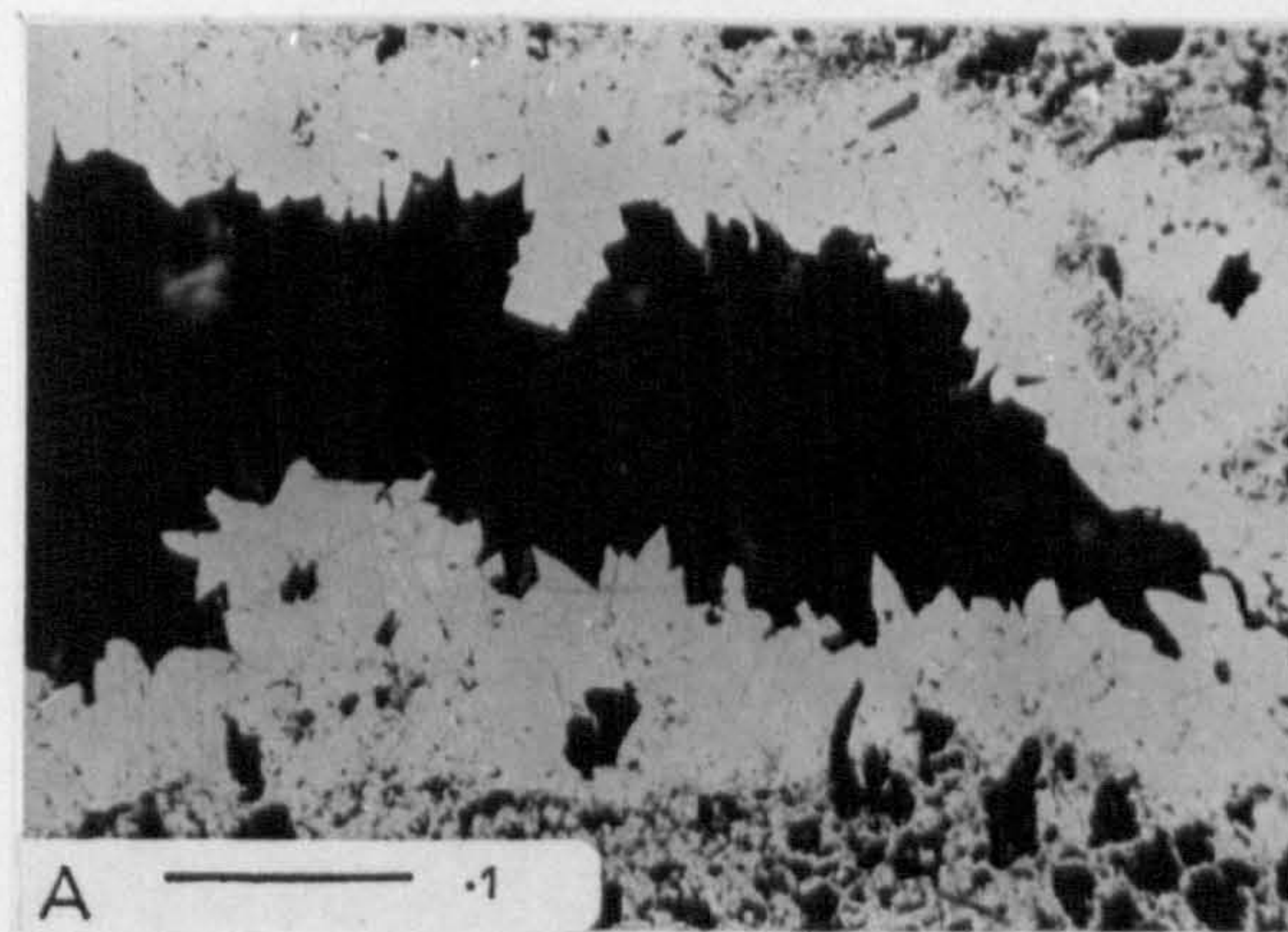




FIGURE 6

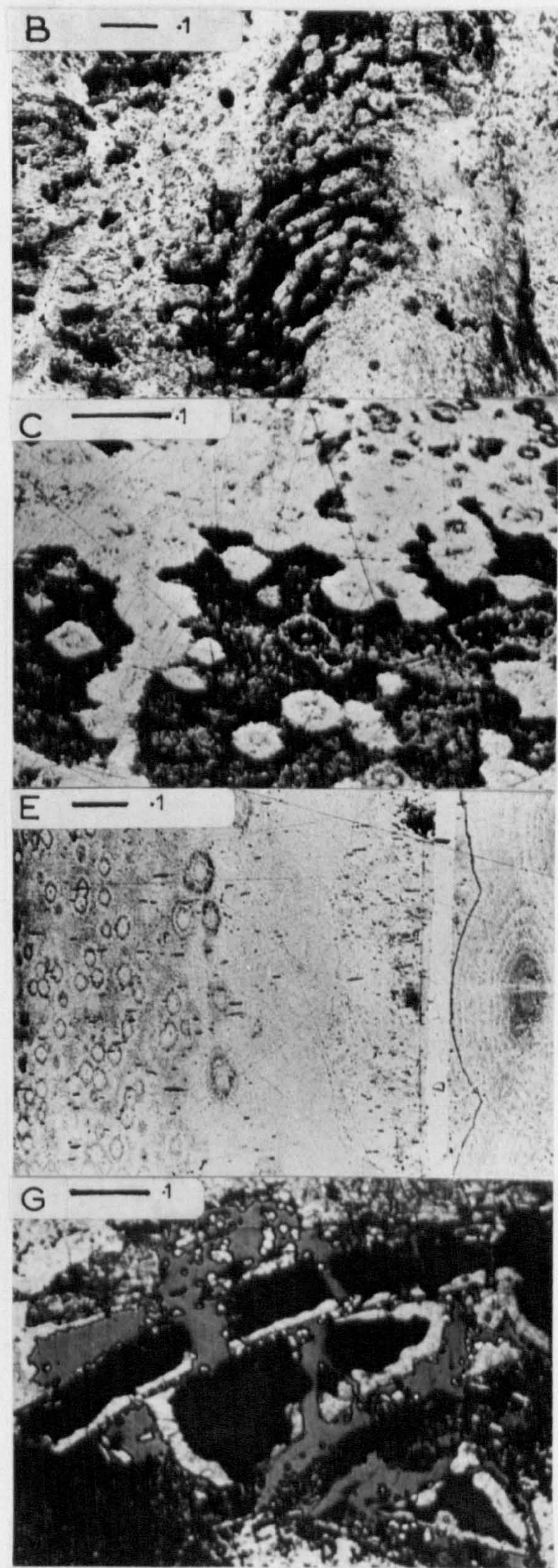
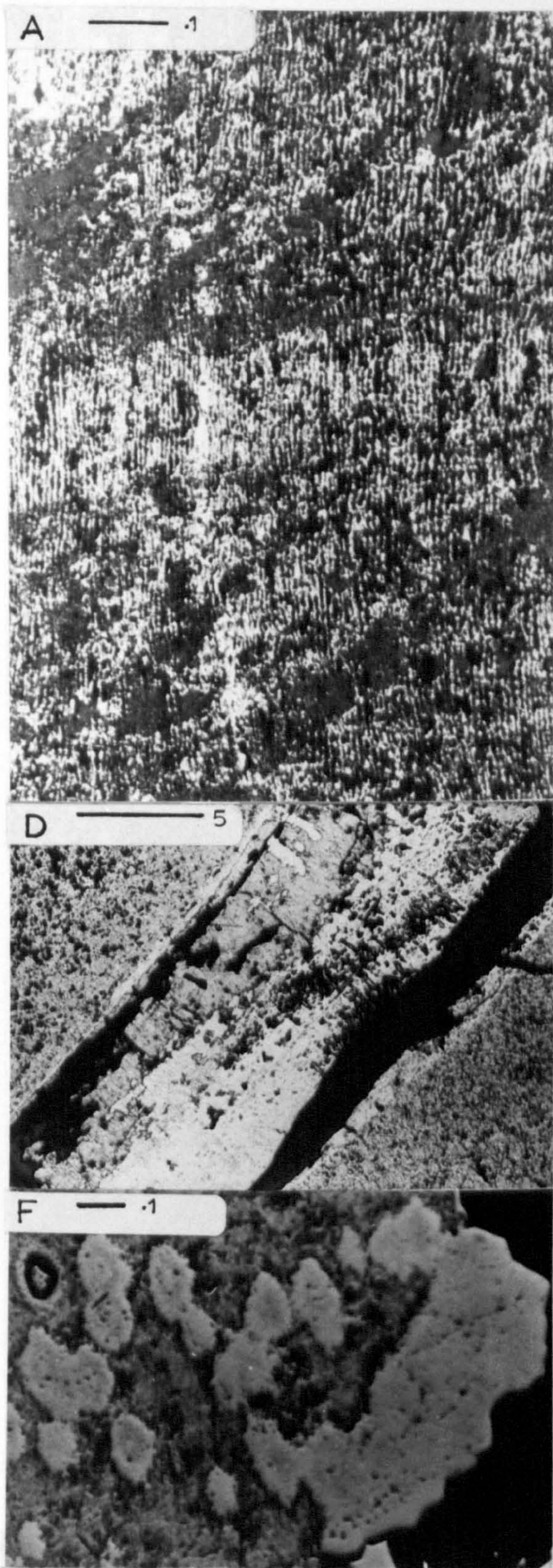




FIGURE 7

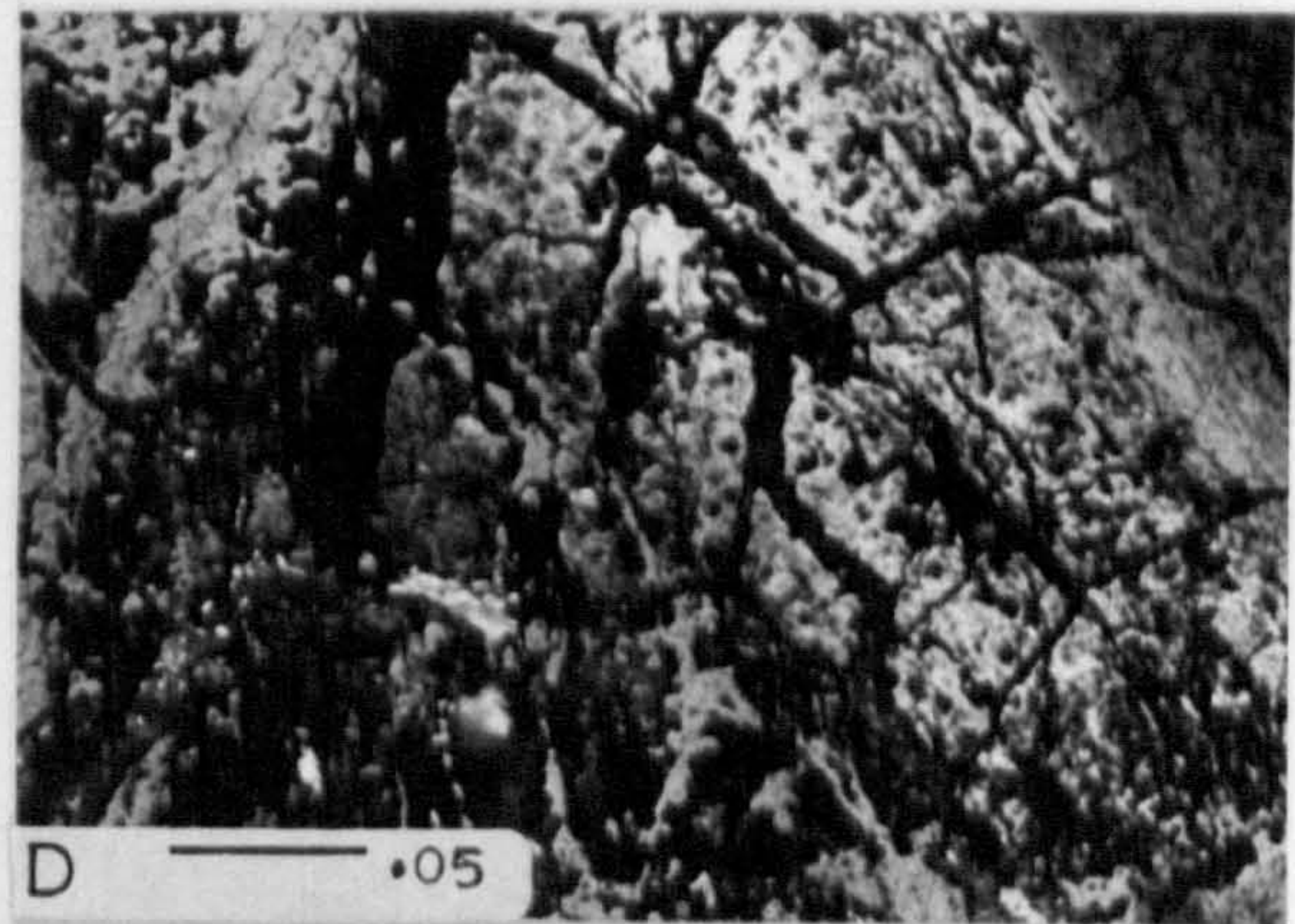
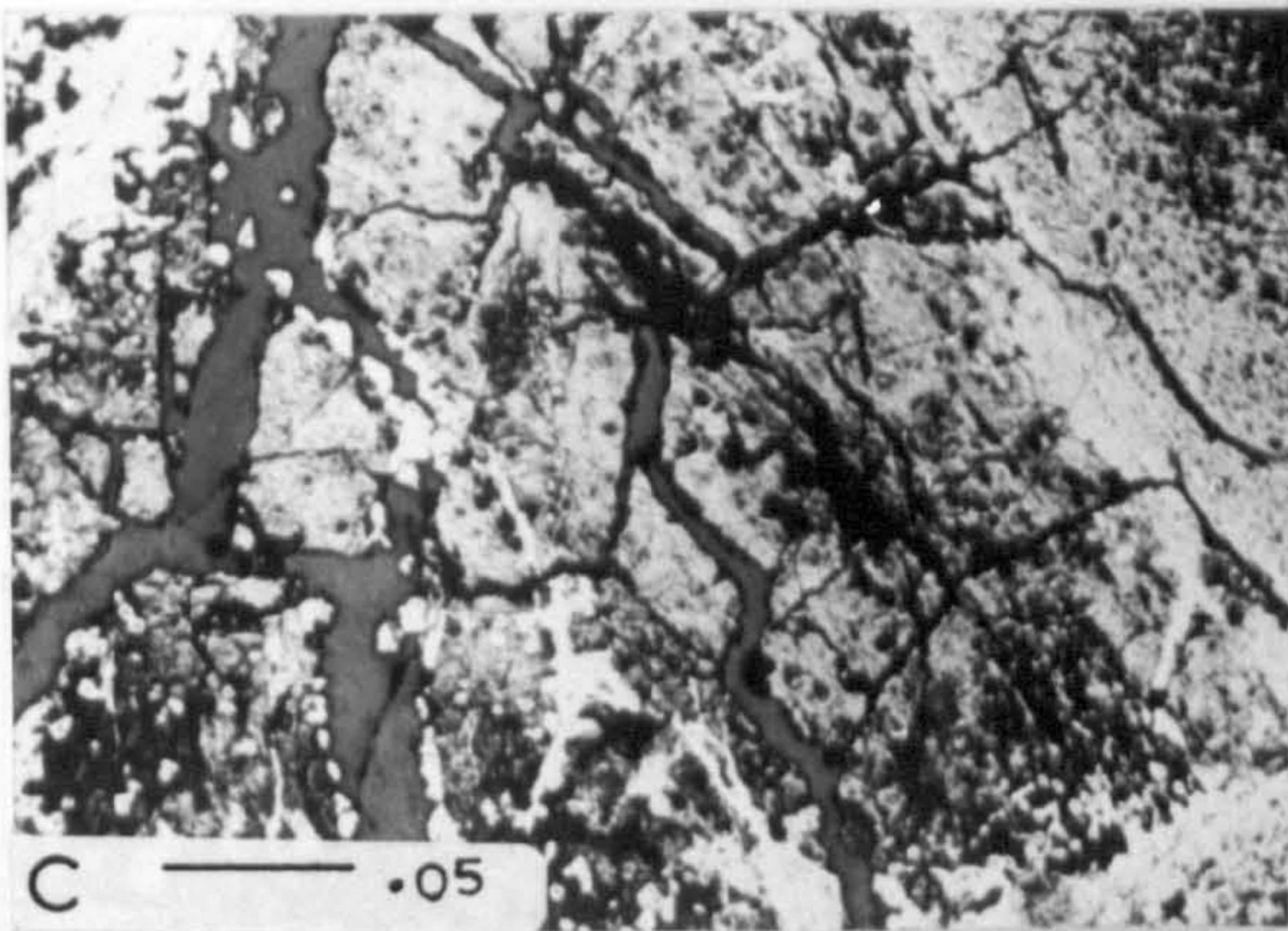
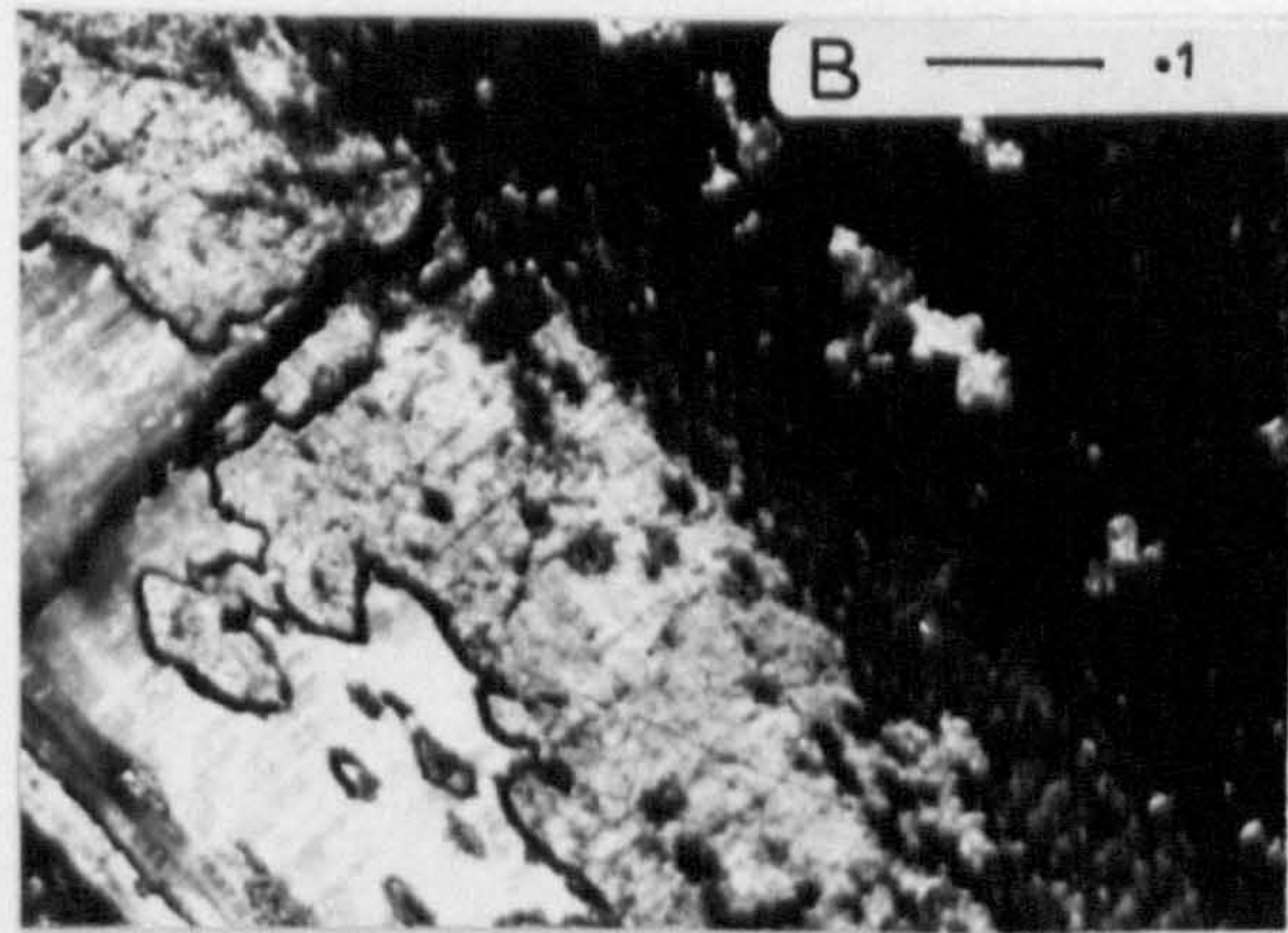
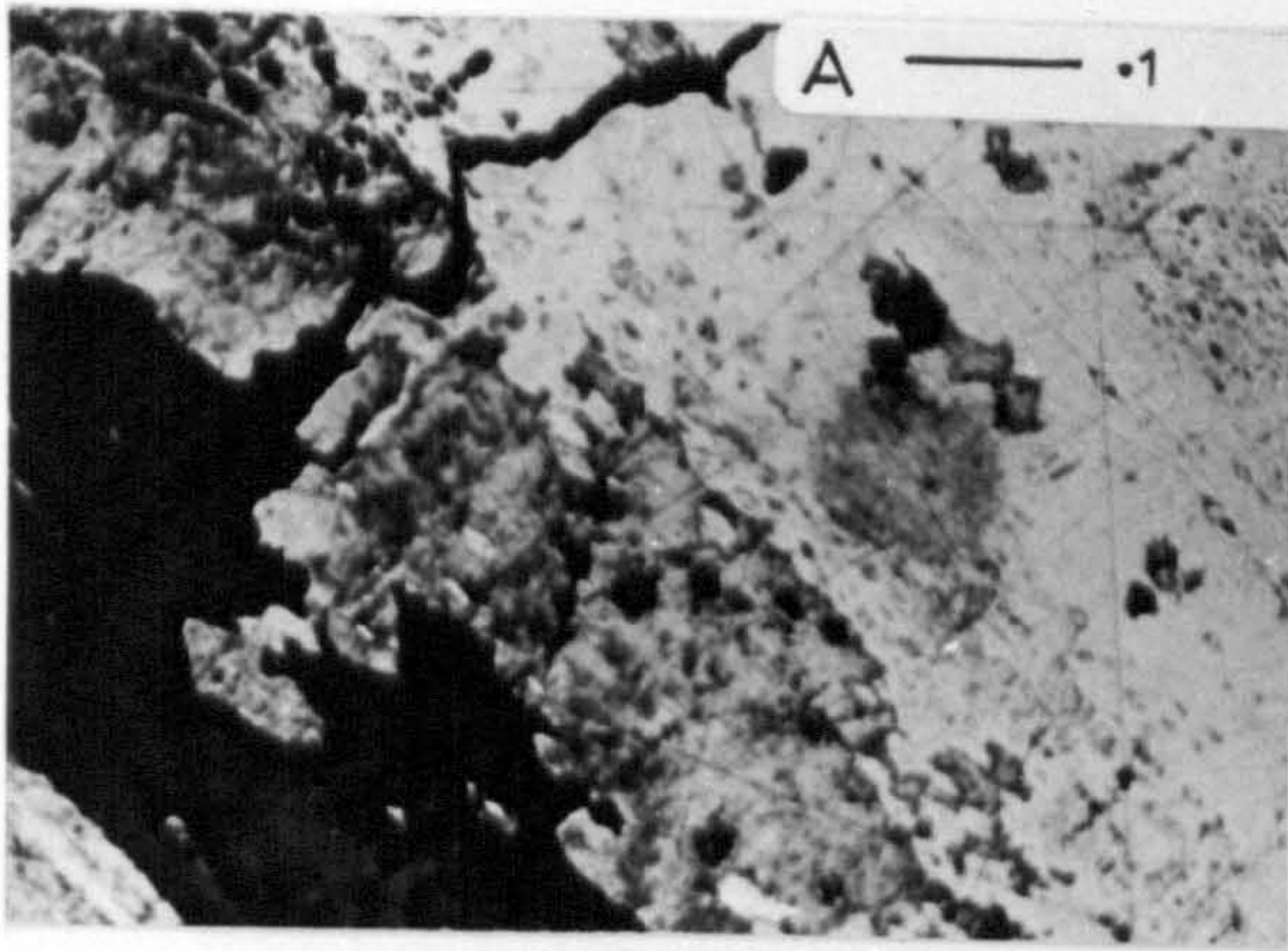


FIGURE 9

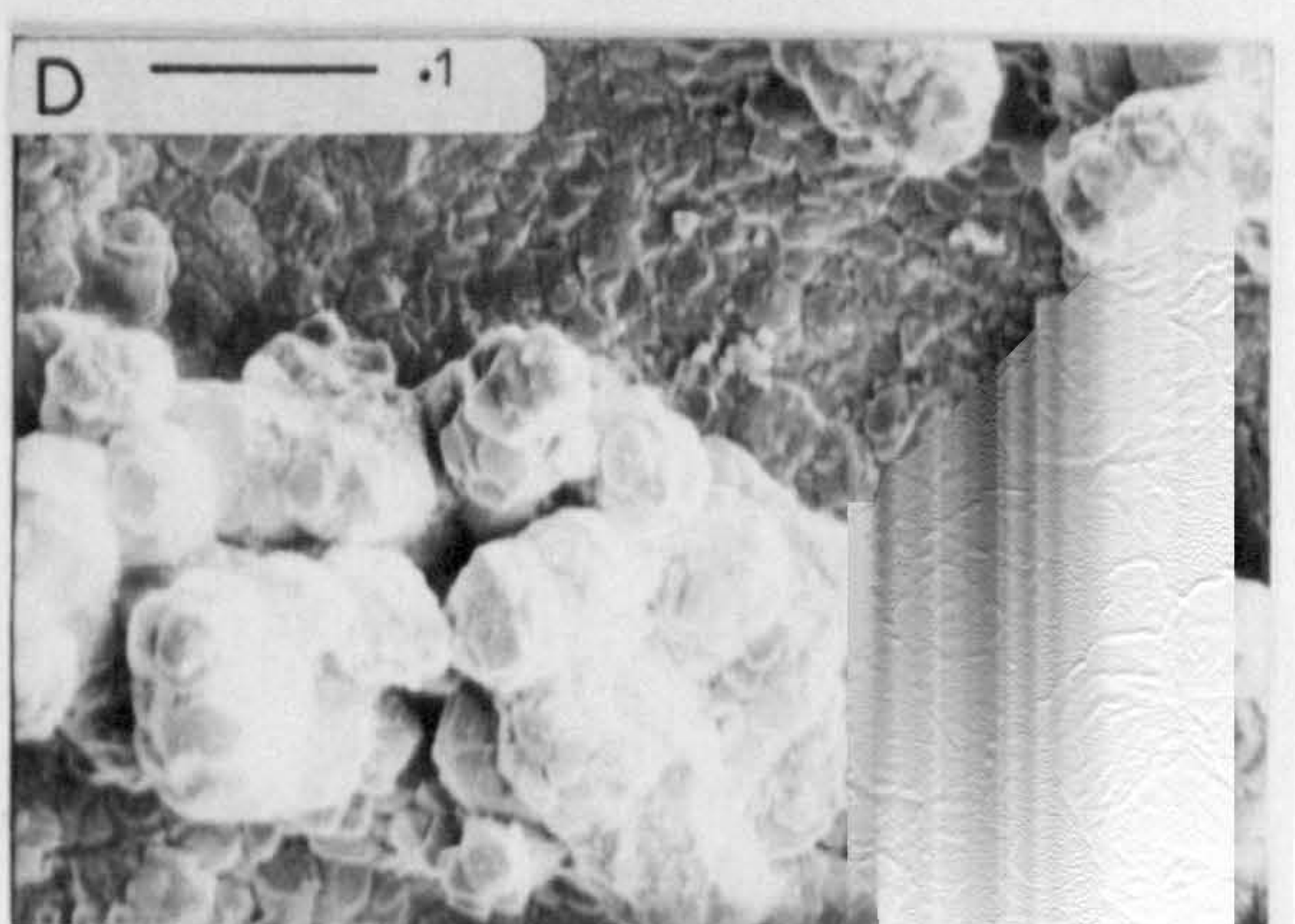
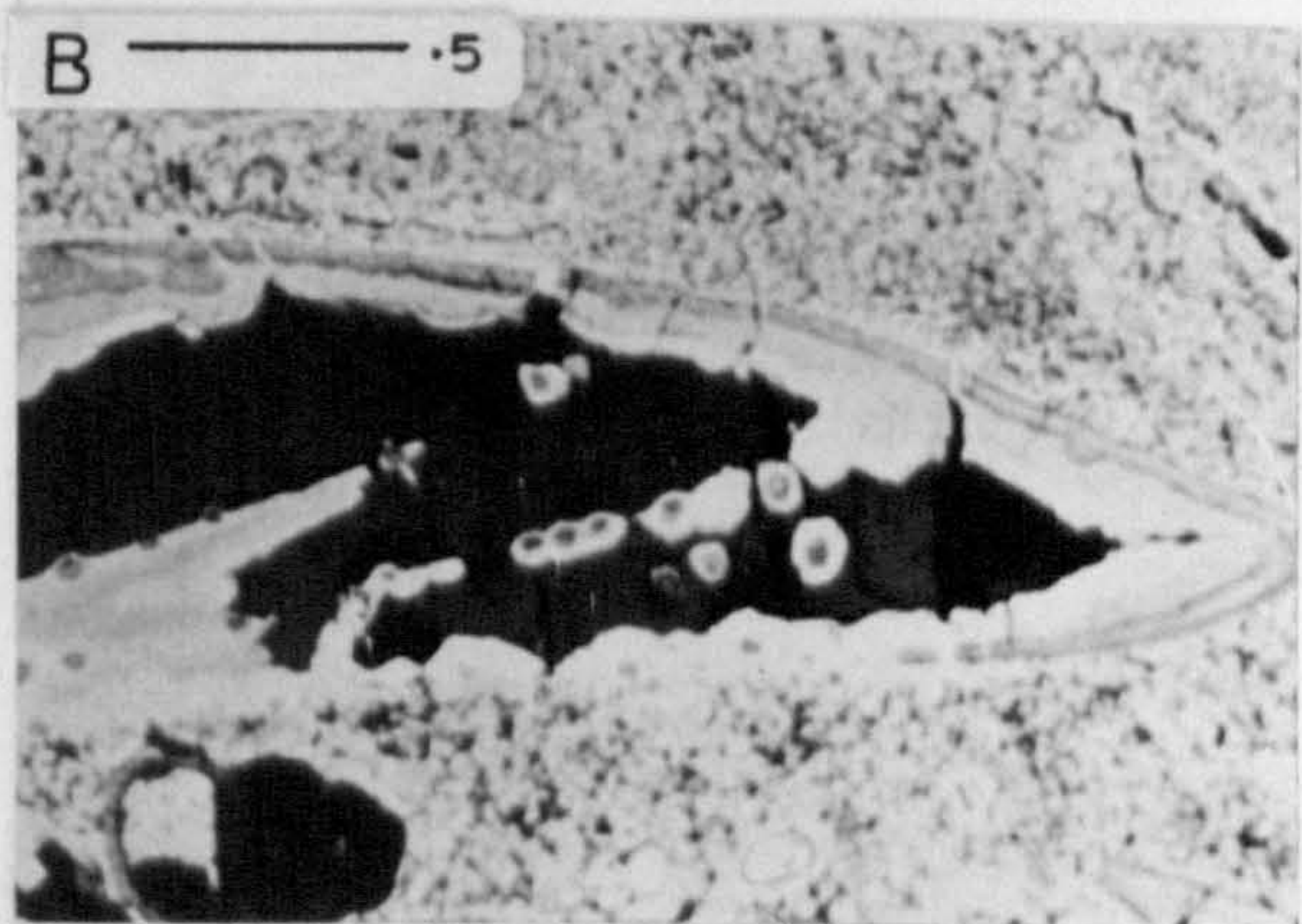
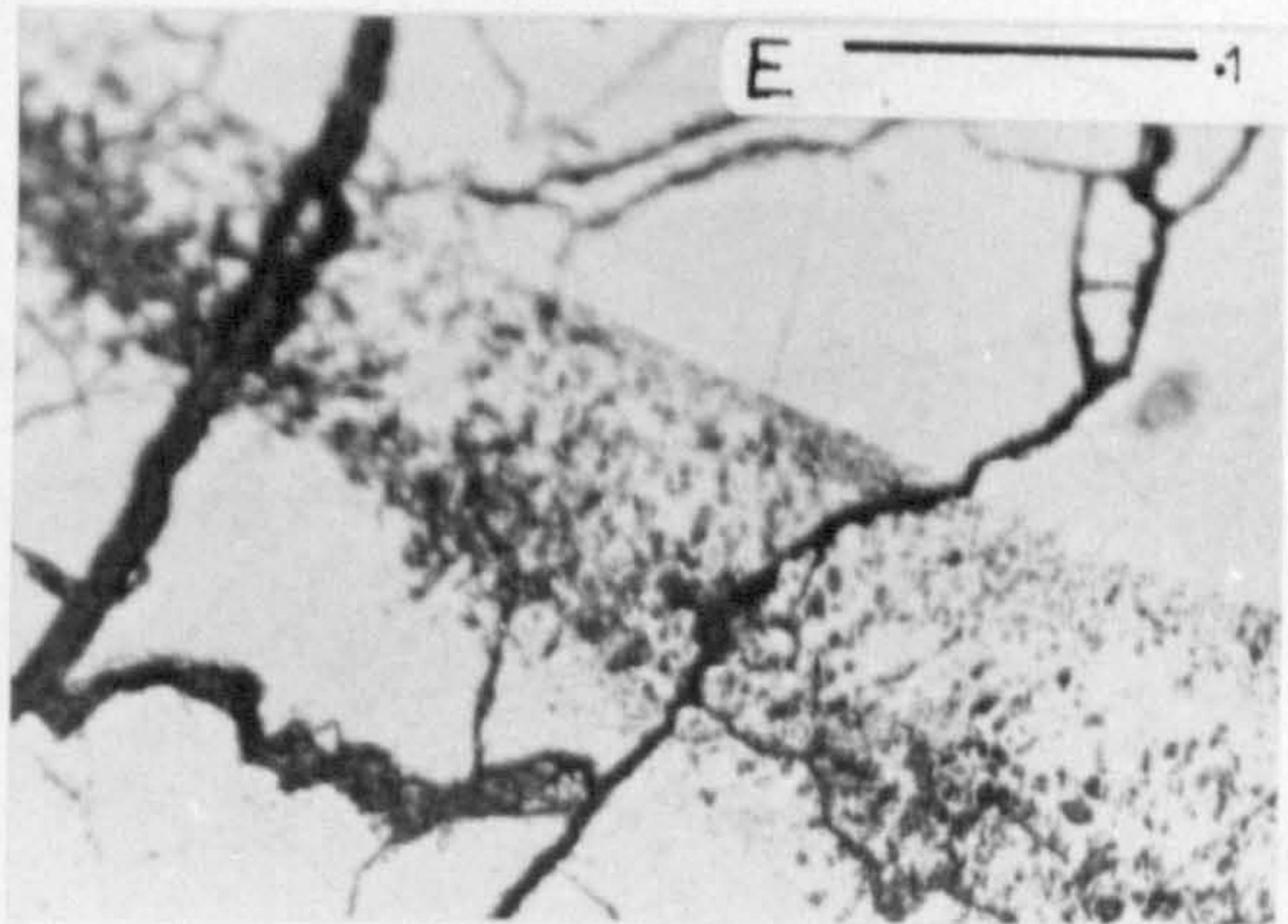
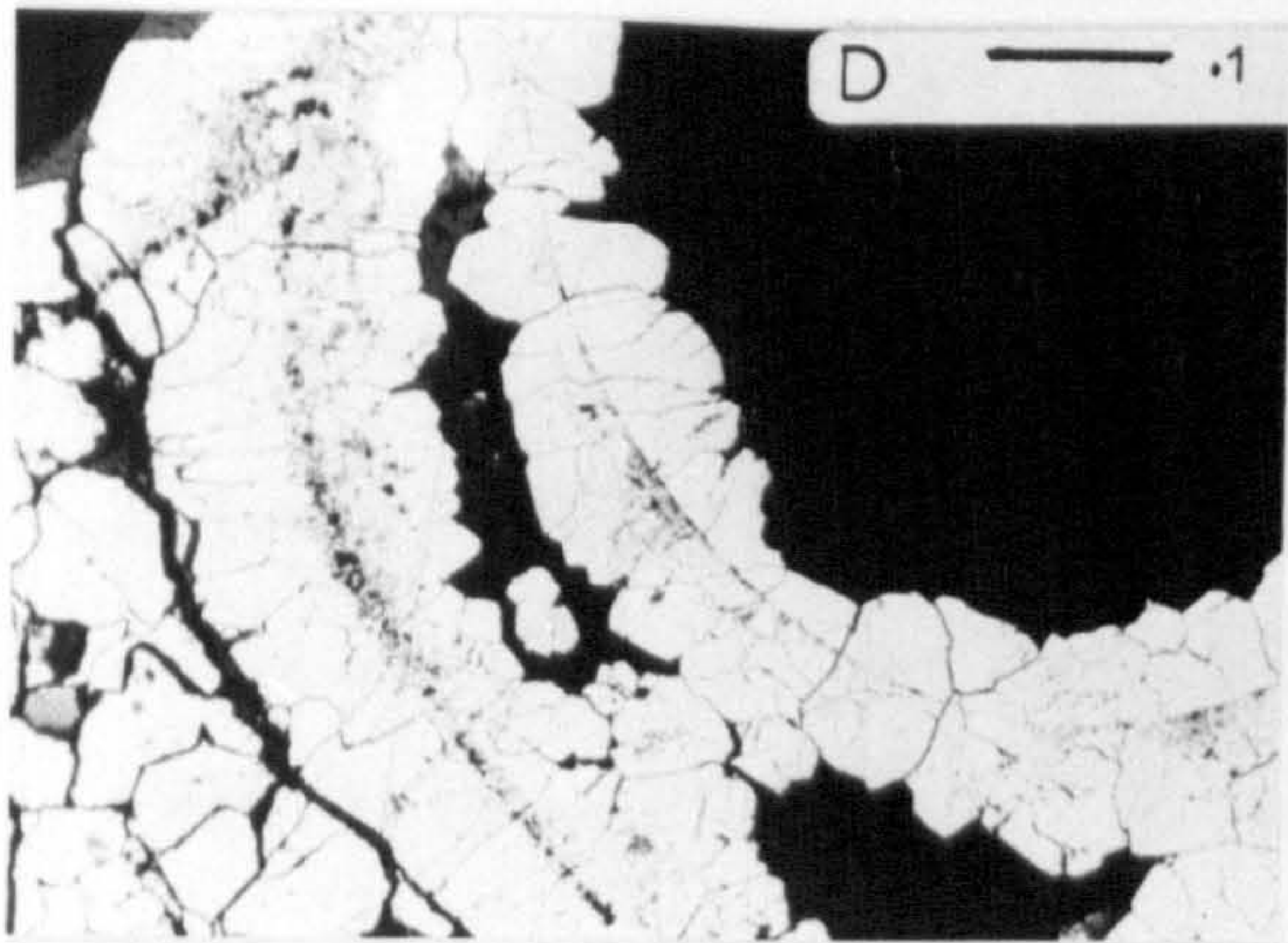
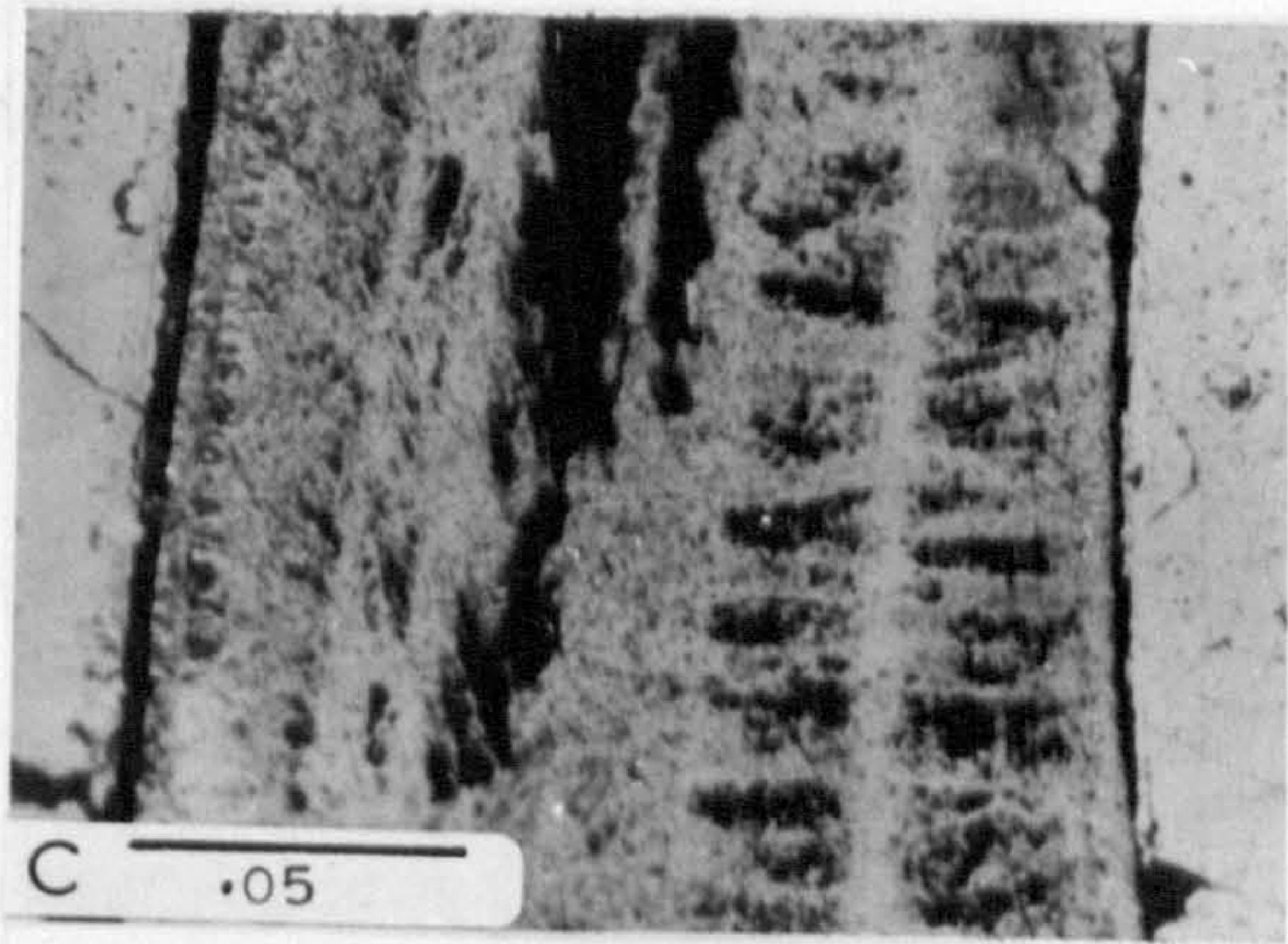
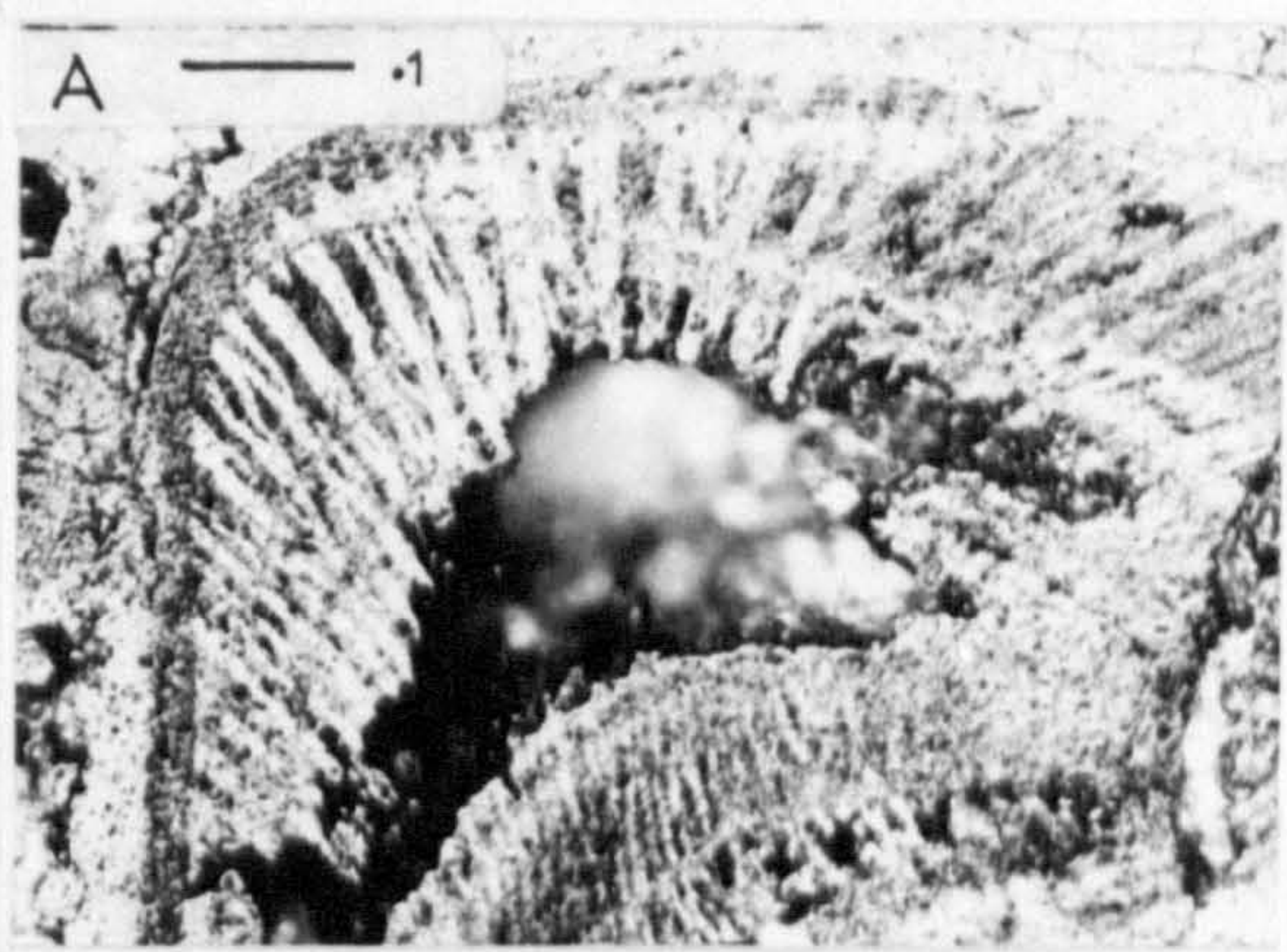




FIGURE 8





General Conclusions

In the previous chapters it has been demonstrated how the  $^{34}\text{S}$  and pyrite contents of Jurassic shales can be used in interpreting the environment of deposition and how these parameters relate to the general biofacies of Morris (1980).

Normal shales, the Upper Oxford Clay and the Dunans Clay, show distinctly low organic carbon and pyrite sulphur contents (<2% and 1.3% respectively) and light (generally <-28‰)  $\delta^{34}\text{S}$  values. The majority of the pyrite in these shales is formed in the surface layers of the sediment where bioturbating organisms mix the sediment with overlying water. The formation of pyrite is limited by the availability of organic matter, a large proportion of which is consumed by aerobic oxidation. The juxtaposing of aerobic and anaerobic environments in the bioturbated portion of the sediment allows reduced sulphide to become reoxidised and serve as a source of isotopically light sulphate. This can result in the sulphide produced having anomalously light  $\delta^{34}\text{S}$  values compared to seawater and the fractionations found in experiments. The source of organic matter plays an important role in the final C/S ratios. When the sediment contains a large proportion of organic matter derived from land plants the C/S ratios are larger than

normally encountered in other parts of the sediment. This is due to the less metabolisable nature of land derived organic material, which contributes a smaller proportion of its total carbon content to the formation of pyrite sulphur.

In Restricted shales, The Lower Oxford Clay, the formation of pyrite appears to be limited by the diffusion of sulphate into the sediment. The surface bioturbated portion of the sediment is more limited than in the Normal facies, and the zone of sulphate diffusion plays a much more important role in the formation of pyrite. The resulting isotopic composition of the fine-grained pyrite lies between -28‰ and -10‰. The fine-grain pyrite sulphur content lies between 0.7 and 2% S and appears to be related to the various biofaces revealed by Duff (1975): The supposedly more oxic environments generally contain more pyrite sulphur.

The biofacies also appear to be related to variations in organic and carbonate productivity. The biofacies in the Lower Oxford Clay are not reflected in the variations of  $^{34}\text{S}$  composition. This is due to the interaction of the many factors that can effect the final isotopic composition of pyrite in the sediment. In general terms the pyrite in the Lower Oxford Clay is a mixture of pyrite formed in the upper bioturbated portion of the

sediment at  $\delta^{34}\text{S}$  approximately seawater-5‰ and pyrite formed in the zone of diffusion at  $\delta^{34}\text{S}$  seawater-25‰, with a small proportion of pyrite formed from sulphate trapped on burial at seawater values. The amount of sulphide formed in the zone of diffusion is limited by the diffusivity of the sediment and the concentration of sulphate in the overlying water. Variations in the isotopic composition probably result from non steady state conditions, due to small scale variations in sedimentation rate, extent of bioturbation etc.

Bituminous shales, the Posidonia and Dunans Shales, generally contain >2% fine grained pyrite sulphur. They have variable  $\delta^{34}\text{S}$  values which relate to the extent of anoxia in the water column and the initial organic input into the zone of sulphate reduction. On the sulphur isotopic composition Bituminous shales can be divided into two types,

1. Those with light  $<-28\text{‰}$   $\delta^{34}\text{S}$  values which indicate sulphate reduction limited by available organic matter.
2. Those with heavy  $>-28\text{‰}$   $\delta^{34}\text{S}$  values indicating a limitation of sulphate reduction by the diffusion of sulphate.

The former corresponds to the Dunans Shale and the latter to the Posidonia Shales. High Degrees of Pyritization in the Posidonia Shale indicate a limitation of pyrite formation by iron. Limitation of



iron results in higher than expected C/S ratios due to the lack of trapping of all the reduced sulphide as pyrite. The heavy  $\delta^{34}\text{S}$  ratios in the Posidonia Shales suggest that interpretations of the environment of deposition which involves extensive stagnation of the water column are not totally applicable, and that an interpretation suggesting a limited, one metre or so, extent of anoxic water with a large amount of reduction occurring in the sediment is more applicable. The light  $\delta^{34}\text{S}$  values in the Dunans shale suggest that an interpretation of the environment involving extensive stagnation is more applicable in this case.

The study of the pyrite replacement of mollusc shells in the Lower Oxford Clay indicates how these represent complicated microenvironments. The particular forms that the replacements take appear to relate to the character of the microenvironment within the general environment of the sediment. Petrographic examination shows that the replacement of the shell is initially dependent on the access of iron and sulphate into the shell by diffusion. Early faithful replacements of the shell probably depend on a limited availability of iron probably due to the general oxic nature of the sediment during the early phases of replacement. The early stages of replacement are characterized by  $\delta^{34}\text{S}$  values between -8 and +18‰. These values are significantly heavier

than the general fine-grained pyrite in the sediment due probably to a combination of lower fractionation factors and the diffusion of the sulphate into the shell. The later stages of replacement are promoted by the crushing and fracturing of the shell. The later stages of replacement do not generally show the faithful replacement of shell structure seen in the early stages. This is probably due to iron becoming more available as the sediment becomes totally anoxic on burial. The late timing of these replacements is indicated both by the petrography and by the characteristically heavy (up to +4‰)  $\delta^{34}\text{S}$  values of the shell replacement and associated concretionary pyrite. The forms of replacement are very much dependent on the general environment of the sediment. This is indicated by the distinctly different preservational types seen in the more and less muddy shell bed horizons.

Sulphate reduction is only one of the many early diagenetic reactions that occur in sediment. It is though linked to many other early diagenetic reactions. As seen, the extent of sulphate reduction occurring in sediments is affected by the amount of aerobic oxidation reduction zone. The extent of sulphate reduction in turn effects the amount and nature of the organic matter passing into deeper diagenetic zones and eventually into the hydrocarbon window. More information on the effects



of the other (oxic, post-oxic, and fermentative) zones can be obtained by the study of the formation of other minerals, such as phosphates, glauconite and carbonate. The work of Benmore et al (1983) has revealed some of the factors which affect the formation of francolite, and its link with sulphate reduction. Combinations of such studies with work on coexisting pyrite and phosphate, as is found in the Dunans Clay or the Speeton Clay (Lower Cretaceous, Yorkshire), may yield useful information on the formation of phosphate and the effects of sulphide reoxidation on the sulphur isotopic composition of pyrite.

This study has produced much data on the variation of pyrite contents and sulphur isotopic composition of ancient shales, the relationships between these factors and the limiting factors of pyrite formation, organic carbon sulphate and iron, and the different shale biofacies. Sulphate reduction and pyrite formation is only one aspect of the early diagenesis of shales and not only shales, but all other types of sediment. This thesis has in some ways only scraped the surface of the problem and there are opportunities to extend this kind of approach to shales of different ages, to other types of sediments, and to link the studies with organic geochemical, palynological studies or with kerogen-typing and maturity analyses.

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### A method For The Determination of Carbonate And Organic Carbon.

This method is based on the production of carbon dioxide either by the action of phosphoric acid on carbonate, or by the oxidation of reduced organic carbon with chromic acid. In both cases the carbon dioxide produced is carried in a stream of air and bubbled through barium hydroxide solution of known strength and precipitated as barium carbonate. After the complete removal of carbon dioxide, the barium hydroxide is back titrated against hydrochloric acid of known strength and the quantity of barium hydroxide which has reacted and hence the amount of carbon dioxide can be calculated.

Similar methods have been described by Bush (1970) and Dixon (1934) but its origins go much further back. The method described below was designed and set up by G.W. Saville at Leicester University. The carrier gas ( $\text{CO}_2$  free air) is re-circulated through the system by means of an electric diaphragm pump. This eliminates the use of several absorption vessels to ensure the complete adsorption of all carbon dioxide.

#### Apparatus

The apparatus is shown in fig(1) and is predominantly

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constructed of Quickfit interchangeable glass ware. The purpose of the various items is as follows.

The **Primary Reaction Vessel** contains the weighed sample which is slightly wetted, and the reagents, either phosphoric acid or chromic acid, are added from the dropping funnel shown.

The **Secondary Reaction Vessel** contains chromium-trioxide in orthophosphoric acid with a mercuric oxide catalyst and is heated to  $130-140^{\circ}\text{C}$ . This ensures complete oxidation of any volatile carbon compounds evolved and hydrogen sulphide which may be produced.

The **Liebigs Condensors** ensure the return of evolved water back into the reaction vessels. Without these the mixture can become very thick and difficult to remove from the flasks. They also serve to prevent water vapour condensing in other parts of the apparatus and so restricting the air flow.

The **Copper Sulphate U-tube** provides an additional safeguard and a visual indicator of the presence of hydrogen sulphide (turning black).

The **Bladder** acts as a cushion to prevent excessive pressure build up in the system. It may also act as an indication of any leaks in the circuit as when such occur the bladder will rapidly become turgid and indicate that the analysis will be suspect.

Reagents.

**Phosphoric acid:** 75% orthophosphoric acid A.R.

**Chromic acid:** Saturated solution of chromium trioxide A.R. in water.

**Chromic acid, mercuric oxide, oxidizing solution:** 4g of chromium trioxide A.R. 0.1g mercuric oxide A.R. in 40ml of 75% orthophosphoric acid A.R.

**0.2N hydrochloric acid solution:** 37ml conc A.R. hydrochloric acid made up to 2l with water. Standardised against di-sodium tetra-borate.

**0.1N barium hydroxide:** 109.5g A.R. barium hydroxide ( $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ ) dissolved in water and made up to 6l in an aspirator bottle. Allowed to stand for 24hr. The clear supernatant liquid is standardised against the hydrochloric acid solution.

**Di-Sodium tetra-borate:**  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , purified according to the method of Vogel (1961).

**Thymol Phthalein indicator**

**Methyl Red indicator.**

Procedure

Determining the Normality of the Hydrochloric Acid

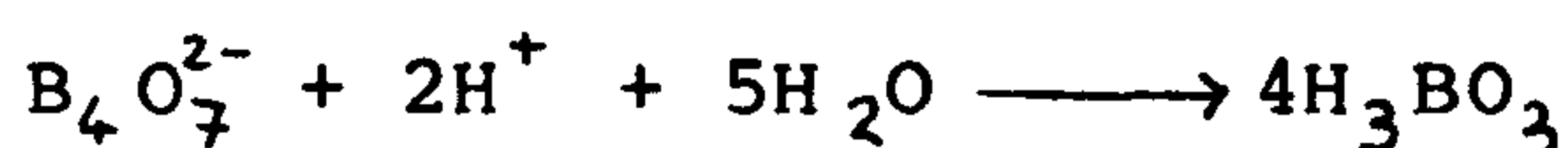
A conical flask is weighed. Di-sodium tetra-borate (about 1g) is added and the flask reweighed. Sufficient water is added to bring the salt into solution (warming



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if necessary). Three drops of methyl red indicator are added. The HCl is added from the burette until the colour changes from yellow to pink.

### Calculation Of Normality



Equivalent weight of  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} = 190.72$

Vol HCl = 28.00

Weight Flask = 71.7755g

Weight Flask +

$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} = 72.7929\text{g}$

Weight of

$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} = \underline{1.0174\text{g}}$

$$\text{Normality HCl} = \frac{1.0174 \times 1000}{190.72 \times 28.00} = 0.1905\text{N}$$

### Determination of the Equivalent Volume of HCl for Ba(OH)<sub>2</sub> Solution

In this method it is not necessary to calculate the exact normality of the Ba(OH)<sub>2</sub> solution, only to know the equivalent volume of HCl required to neutralize the known amount of Ba(OH)<sub>2</sub> used in the absorption vessel. Therefore, 50ml of CO<sub>2</sub> free water and 50ml of Ba(OH)<sub>2</sub> solution with 6 drops of thymol phthalein indicator are added to the absorption vessel. This is then incorporated in the closed circuit system without any sample present. The system is then switched on and treated as in the normal procedure, including heating the secondary reaction vessel to 130-140°C. After 20 minutes the adsorption vessel is removed and its



contents back titrated against the hydrochloric acid and the result recorded.

### Standard Operating Procedure.

Before beginning any determination, the air in the system must be CO<sub>2</sub> free. This is done by connecting a U-tube of soda lime in place of the adsorption vessel and a link tube in place of the primary reaction vessel. Whilst the gas is circulating the sample may be weighed.

The primary reaction vessel is weighed . The sample (0.3 to 0.7g depending on the carbon content) is added by means of a clean glass funnel. The vessel is then reweighed and the weights recorded. A few drops of water are added to dampen the sample and prevent it floating on the viscous phosphoric acid. The following procedure is then followed.

1. Pump switched off.
2. Reaction vessel with sample inserted in circuit in place of the link piece, pump switched on.
3. Contents of the secondary reaction vessel heated to 130-140°C.
4. CO free water and 50ml Ba(OH)<sub>2</sub> solution with 6 drops of thymol phthalein indicator added to the major adsorption vessel. 15ml Ba(OH)<sub>2</sub> solution added to the minor adsorption vessel.

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5. Pump is switched off and absorption vessels placed in circuit.
6. Pump switched on.
7. 10ml of phosphoric acid is delivered to the dropping funnel by means of a 10ml syringe.
8. The phosphoric acid is slowly added to the reaction vessel and the vessel is shaken (within the limits of the apparatus) and heated gently.
9. Heating and shaking is continued for at least 20min or until all the carbon dioxide has precipitated. To check this the gas flow may be directed through the minor adsorption vessel by turning the two way valve and opening the clip. If the solution starts to cloud the tap is turned back to the main vessel. The two solutions are combined when they are back titrated.
10. Pump is switched off and the absorption vessel removed and replaced by the soda lime U-Tube. The contents of the vessel are then back titrated against the HCl to give the carbonate carbon content.
11. The absorption vessels are refilled and replaced in the circuit.
12. The pump is switched on.
13. 6ml of chromic acid are added to the sample

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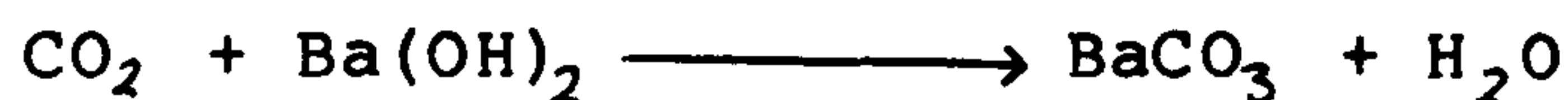
phosphoric acid mixture in the reaction vessel and the procedure is continued as before to determine the organic carbon.

### Calculation of Results.

#### Known Quantities.

Normality of hydrochloric acid	=	N
Equivalent volume of hydrochloric acid for 50ml Ba(OH)	=	V1
Volume of acid used in back titration	=	V2
Weight of sample	=	W

#### Equations



2 moles of acid react with 1 mole of Ba(OH)<sub>2</sub>

No. moles of Ba(OH)<sub>2</sub> in absorption vessel at start of determination

$$= 1/2 \text{ N}/1000 \times \text{V1}$$

No. of moles of Ba(OH) after determination

$$= 1/2 \text{ N}/1000 \times \text{V2}$$

As 1 mole of CO reacts with 1 mole of Ba(OH) the number of moles of CO liberated = number of moles of

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Ba(OH) used during the determination

$$= 1/2 N/1000 (V1-V2)$$

hence, either

$$\%CO_2 = \frac{44.01 \times N \times 100 \times (V1-V2)}{W \times 2 \times 1000} \quad (\text{For Carbonates})$$

$$\text{or } \%C = \frac{12.01 \times N \times 100 \times (V1-V2)}{W \times 2 \times 1000} \quad (\text{For Carbonates or organic carbon})$$

therefore

$$\%CO_2 = 2.2005 \times N/W \times (V1-V2)$$

$$\%C = 0.6005 \times N/W \times (V1-V2)$$

If more than 50ml of Ba(OH) is used in the absorption vessels, then:

$$\text{Equivalent Volume of HCl} = \frac{\text{Volume Ba(OH)}_2 \text{ Taken} \times V1}{50}$$

### Example

Normality of Acid = 0.1988 N

Equivalent Vol.HCl

to 50ml Ba(OH)<sub>2</sub> = 28.40 ml

Weight Vessel = 73.2456g

Weight vessel

+Sample = 73.8877g

Weight Sample = 0.6421g

### Carbonate

Vol. Ba(OH)<sub>2</sub> taken = 80ml



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Vol HCl in back titration = 40.30ml = V2

$$V1 = \frac{80 \times 28.40}{50} = 45.44$$

Therefore

$$\begin{aligned} \%CO_2 &= \frac{2.2005 \times .1988}{.6421} \times 5.15 \\ &= \underline{3.50\%} \end{aligned}$$

### Organic Carbon

Vol Ba(OH)<sub>2</sub> taken = 76ml

Vol HCl in back titration = 15.4 =V2

$$V1 = \frac{76 \times 28.40}{50} = 43.16$$

Therefore

$$\begin{aligned} \%C &= \frac{.6005 \times .1988}{.6421} \times 27.76 \\ &= \underline{5.16\%} \end{aligned}$$

### Results.

A sample of analar calcium carbonate was analysed three times using the above method and yielded a result of

$$43.94 \pm 0.54 \text{ (2 std dev.) } \%CO_2$$

this compares with the value of 43.97% for 100% pure calcium carbonate.

One sample of organic-rich shale was run six times to assess the variation of result.

%C organic	%C Carbonate
3.19	2.38
3.20	2.42
3.19	2.41
3.15	2.35
3.24	2.34

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	3.07	2.33
means	3.17	2.37
2 x Std Dev.	0.11	0.08

The method can therefore be seen to give both accurate and precise values.

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APPARATUS FOR DETERMINING CARBONATE CARBON  
AND ORGANIC CARBON

