# **BLACK SHALES**

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## Preface

Black shales have attracted interest from geologists for many reasons, not least of which is their economic importance as the source of most of the world's petroleum. The study of black shales has therefore proceeded with considerable impetus, particularly over the last two decades. Their study is particularly facilitated by the extremely wide range of geological disciplines that have been utilized, from organic geochemistry to palaeoecology. It is therefore rather surprising that, with an increasingly large and diverse data set, we appear to be raising more questions than we are answering. Part of this problem stems from the disparity of the data and the often too narrowly focused scope of many studies. None the less, the range of mutually contradictory models and theories concerning all aspects of petroleum source rocks is startling, and it is clear that many of the ideas expressed in the black shale literature must be wrong.

Black shales is not infended to be a higher-level undergraduate textbook as this would have to contain, by definition, a synthesis of current dogma. As I have already hinted, there is very little dogma to present. Rather I have aimed to provide a partisan review text of the numerous on-going debates in the field, focusing particularly on the apparently irreconcilable debate between those favouring high productivity and those who prefer enhanced preservation for black shale formations. A secondary aim has also been to draw together for the first time the disparate knowledge available in this field. In order that the book be accessible to more than just black shale specialists I have, where necessary, included reviews of essential background information and terminology.

The views and ideas expressed in this book have been developed and modified over the years in conversation and letters with numerous colleagues, particularly James Maynard, Tony Hallam. George Grabowski, Richard Tyson, Dave Martill, John Hudson, Keith Myers, and Brad Sageman. I am especially grateful to the small team of patient reviewers of earlier drafts of the manuscript, James Maynard, Jane Francis, Jim Best, Rob Raiswell, Simon Dean, and Andy Holmes.

Leeds University July 1993 P. B. W.

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#### **1.1 INTRODUCTION**

Black shales are of enormous economic importance because they source the bulk of the world's hydrocarbons and yet they are amongst the least understood of all sedimentary rock types. Black shales lend themselves to study by a broad range of geological disciplines including sedimentology, palaeoceanography, palaeoecology, palynology, inorganic and organic geochemistry and, more recently, stratigraphy. Despite this activity, there is little consensus concerning any of the requirements for black shale formation. Less than 20 years ago Cane (1976, p. 27) was of the opinion that, 'any consideration of the origin and mode of formation of oil shale [i.e. black shale] must be, with little exception, highly speculative.' Recently Bralower's (1992) more optimistic assessment was that 'By the 21st century, these fascinating deposits will no longer be one of the major stratigraphic enigmas.' We shall see.

The long-established black shale epithet has been used for a broad variety of rock types in the literature, commonly without any specific definition. Tyson (1987) defined black shales as, 'dark-coloured, fine grained mudrocks having the sedimentological, palaeoecological and geochemical characteristics associated with deposition under oxygen-deficient or oxygen-free bottom waters.' This useful genetic definition is adopted here although it is important to note that many palecoloured carbonate petroleum source rocks probably formed under similar conditions and they too are considered here. Some studies use black shale interchangeably with genuinely descriptive terms such as organic-rich shale and bituminous shale (e.g. Stow, 1987). However, at least some fine-grained strata, deposited under anoxic or oxygen-deficient conditions, are not organic-rich (e.g. Kemp, 1991; Wignall and Hallam, 1992). It is therefore desirable that the degree of organic richness is not used in the definition of black shale.

A plethora of terms is available for the description of oxygen-poor environments and their current use is rather confusing. For example, 'Far too many papers casually equate "anoxic" with "oxygen deficiency" or define their own limits.' (Tyson, 1987, p. 56). Two distinct terminologies are to be found in the geological literature. Marine biologists and geochemists use a scheme with '-oxic' endings defined by precise, measured oxygen values or implied oxygen values in ancient settings (Fig. 1.1). The remainder of the geological fratemity, and particularly palaeoecologists, use a tripartite '-aerobic' terminology proposed by Rhoads and Morse (1971). These authors synthesized a data set for modern oxygen-deficient marine environments in which measured oxygen values were available. However, the various boundaries within the scheme are defined by characteristic faunal and sedimentological changes. This is a biofacies classification scheme although many subsequent authors have incorrectly used the term to describe environmental oxygen levels.

Both the environmental and biofacies schemes have undergone considerable modification over the past two decades (Fig. 1.1; see discussion in Chapter 3). The

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ENVIRONMENTAL Oxygen levels	27	oxic	suboxic		dysoxi	ic	охіс
OXYGEN-RESTRICTED BIOFACIES (ORBs)	1	2	3	4	5	6	
BIOFACIES TERMS	anad	erobic	ex	aerobic	dysaero	bic	aerobic

Fig. 1.1. Terminology of oxygen-restricted environments and facies (cf. Tyson and Pearson, 1991).

environmental scheme should describe inferred, absolute oxygen values at defined positions within the water column or the sediment, such as 'dysoxic bottom waters'. The exception is the useful term 'euxinic' which, by definition, implies anoxic conditions and free  $H_2S$ extending for at least several metres, into the bottom waters. The biofacies scheme essentially relates to oxygen conditions at the sediment/water interface and should only really be used to describe 'solid' geological data such as 'anaerobic shales' or a 'dysaerobic fauna'.

A major difficulty with interpreting black shale depositional environments lies in a lack of recent analogues, particularly of the extensive, thin black shales that are so charactersistic of many Palaeozoic and Mesozoic epicontinental seas (Klemme and Ulmishek, 1991). The present is most certainly not the key to the past in this case. However, this problem is alleviated to some extent by the wealth of multidisciplinary data now available for many black shale units which provides ample scope for palaeoenvironmental assessment.

#### **1.2 BLACK SHALE CONTROVERSIES**

Most sedimentary rocks only contain trace amounts of organic matter, and this is usually highly refractory humic material. In contrast, most black shales are enriched in organic matter, particularly lipids. Therefore one ot the fundamental questions of black shale studies is how lipid preservation occurs.

Pioneering studies of black shale genesis recognized that anoxia inhibits organic matter degradation and that silled basins, such as the modern day Black Sea, commonly have anoxic bottom waters (Pompeckj, 1909; Woolnough, 1937; Section 7.1). Therefore, for the first half of this century, Black Sea conditions were taken as a model for many ancient black shales. The importance of anoxia was founded on the, at that time, untested assumption that anaerobic bacteria are less efficient at degrading organic matter than aerobic bacteria.

Inevitably, subsequent work has viewed this traditional model as an over-simplification. Tyson (1987) listed five factors (discussed below) that he considered to be important controls of organic matter preservation. Whilst the importance of some of these controls is well understood the majority are poorly constrained.

#### 1.2.1 Sediment texture and grain size

Due to their similar settling velocities, clay minerals and particulate organic matter accumulate in the same sites,

generally topographic depressions. The low porosity and permeability of fine-grained sediments tends to enhance organic matter preservation by restricting the contact of organic matter with potential oxidants such as dissolved sulphate and oxygen.

#### 1.2.2 Water depth

Organic matter descending through the water column is subject to oxidation. Therefore, greater transit times will favour greater degradation of the organic matter before its arrival at the sea floor. Transit time is a function of the degree of wind-mixing of the water column (basin size, climate, and palaeogeography may all influence this), particle size, water salinity, and water depth. Generally the transit time is less in shallower water sites. Shallow water models have been proposed for several black shales over the past few decades (e.g. Leckie et al., 1990), particularly the thin Pennsylvanian black shales of the United States (Conant and Swanson, 1961; Zangerl and Richardson, 1963; Coveney et al., 1991). Nonetheless most workers consider that black shales are a deepwater facies (Heckel, 1991; Wignall and Hallam, 1991). Cluff (1981, p. 1029) noted, with justifiable cynicism, that, 'The weight of popular geologic opinion in the deep versus shallow water debate] has shifted back and forth through the years with a cyclicity more likely related to sunspot activity or the passing of some distant comet than to hard, factual evidence.'

The relative depths at which black shales accumulate are perhaps more easily determined by the application of Walther's rule to lateral facies relationships. But such principles have led many authors to suggest very shallow deposition of black shales due to their close association with unequivocally shallow-water facies such as coals. However, the presence of sequence boundaries and flooding surfaces between black shales and shallow-water facies invalidates many, but not all, examples of shallow-water black shales (cf. Chapter 9).

#### 1.2.3 Sedimentation rate

Muller and Suess (1979) proposed that high sedimentation rates enhance organic matter preservation by removing organic material from the near-surface zone of intense bacterial activity. This was based on their data set derived from modern day oxic settings. However, their observed relationship is contradicted by evidence from the geological record which shows that, relative to other facies, black shale accumulation rates are exceedingly slow (Creaney and Passey, 1993; Section 6.3). However, like water depth, we have no way of measuring absolute sedimentation rates and estimates can vary by up to four or five orders of magnitude. For example, Zangerl and Richardson (1963) estimated that the few decimetres of the Mecca Quarry (black) Shale accumulated in four years whilst Heckel (1977, 1991) suggests that this, and other thin Pennsylvanian black shales, probably represent several tens, if not hundreds of thousands, of years worth of accumulation.

Varves (laminations reflecting annual variations in sedimentation) have been used to estimate sedimentation rates but these give consistently high values (e.g. Oschmann (1990) estimated rates greater than 10 cm/ 1000 yrs based on varve analysis) which are rather high for hemipelagic sediments, compared with modern-day values less than 2 cm/1000 yrs. In fact, the supposed presence of varves in most black shales is highly suspect' (cf. Section 2.4).

### 1.2.4 Primary production and rate of organic matter supply to the sediment

Organic matter is generally considered to be sourced by a combination of phytoplankton, land-derived plants and a poorly known input from chemoautotrophic bacteria (Williams and Reimers, 1983). Most lipid-rich organic matter is derived from planktonic organic matter (Tissot and Welte, 1978). The abundance of such material in black shales has led many authors to suggest that they accumulated beneath surface waters with elevated productivity (cf. Chapter 6). Primary productivity is controlled by the supply of nutrients such as nitrogen and phosphorus. At present, the highest nutrient supplies are found in upwelling zones along the western margins of continents and in shelf seas with high runoff from the adjacent land (Demaison and Moore, 1980; Parrish, 1982; Section 7.3). A large supply of organic matter to the sea floor will establish benthic anoxia whilst allowing a significant proportion to survive aerobic and anaerobic degradation-a process known as organic overloading. Organic matter is only preserved by virtue of its over-abundance which overwhelms all available oxidants. This model differs fundamentally from the traditional silled basin model for, in this case the benthic anoxia is merely a consequence of organic matter degradation rather than a cause of its preservation. Calvert *et al.* (1991) stressed that 'anoxic conditions in the water column may not be a prerequisite for the preservation of organic matter in marine sediments.'

Silled basins are nutrient sinks, due to the inhibition of vertical advection by density interfaces, and primary productivity is consequently not very high in such settings (Tyson, 1987). Therefore high productivity is unlikely to be encountered in silled basins and conditions of both high productivity and high preservation are unlikely to be encountered in the same setting, although this is commonly proposed (e.g. Legget, 1980). Such misconceptions are also to be found in textbooks. Wicander and Monroe (1989, p. 288) noted that 'the essential features required to produce them [black shales] include undisturbed anaerobic bottom water, a reduced supply of clastic sediment, and high organic productivity' (my italics).

In Demaison and Moore's (1980) highly influential review of black shale formation they concluded that high productivity was only occasionally a salient factor and many black shale studies have tended to concur. In contrast, Pedersen and Calvert (1990) claimed, with some justification, that organic matter degradation is more efficient under anoxic rather than oxic conditions. They concluded that black shales will only accumulate under surface waters of exceptionally high productivity in oxic settings.

#### 1.2.5 Bottom-water oxygenation

The only common theme in all black shale models is the presence of very low oxygen or truly anoxic bottom waters, although the proposed causes vary (restricted circulation or the decay of abundant organic matter). The detection of palaeo-oxygen levels in the geological past is therefore of prime importance in the assessment of black shales and hydrocarbon source rocks and there has been considerable expenditure of effort towards this aim (cf. Chapters 2 to 5).

# Sedimentology

#### 2.1 INTRODUCTION

Mudrocks consist of clay minerals with minor amounts of organic matter, micrite, and quartz silt. A host of depositional processes have been proposed for mudrock sedimentation including hemipelagic settling, nepheloid flows, turbid plumes, low-density turbidity currents, bottom currents (contourites), and storm currents (Piper, 1972; Stow and Bowen, 1980; Pickering et al., 1986; O'Brien, 1989; Reimers et al., 1990). For the most part these processes involve low current velocities and sedimentary layers are rarely more than a few centimetres thick. In oxic conditions, muds are bioturbated to a depth of at least 10 cm (Wetzel, 1984) and sedimentary structures are destroyed. Only under anoxic or suboxic bottom waters (cf. Fig 1.1) are finescale sedimentary structures preserved due to the inhibition of burrowing. Soutar et al. (1981) have noted that even under dysoxic oxygen levels it only requires 4 to 5 years for burrowers to destroy all sedimentary structures. Therefore the presence of fine-scale structures testifies to the persistent occurrence of anoxic/ suboxic conditions during deposition. Black shales therefore offer an ideal opportunity to study mud depositional processes. However, the processes may be slightly atypical for mudrocks as a whole due to the common presence of density interfaces in the water column of oxygen-restricted basins which can modify depositional mechanisms (see below).

Fine-scale sedimentary structures can also be preserved under conditions of exceptionally high sedimentation rates which 'outpace' the burrowers (Leithold, 1993). Such conditions require unusually high rates, of the order of several metres per thousand years whilst typical black shale accumulation rates appear to be two orders of magnitude slower than this. For example, the thin storm laminae recorded by Pedersen (1985) in a muddy Jurassic succession from Denmark could have accumulated beneath anoxic bottom waters. But, Pedersen notes that the storm beds are located in a mid-shelf setting whilst contemporaneous sediments down-dip are fully bioturbated basinal muds. If anoxia had been the cause of preservation of the laminae then they would most likely occur in the most basinal settings (see Chapter 7). Their mid-shelf position suggests high sedimentation of a storm facies.

Millimetre and sub-millimetre scale lamination is the most ubiquitous sedimentary structure preserved in black shales. These are usually organized into couplets of different composition. Alternating silt laminae and clay mineral/kerogen laminae are the most frequently recorded (Piper, 1973; Cluff, 1980; Wignall, 1989; O'Brien, 1989, 1990; Dimberline et al., 1990) whilst micrite and clay mineral/kerogen couplets (Dickman and Artuz, 1978; Grabowski and Pevear, 1985; Wignall, 1989; Fig. 2.1) and biogenic silica and clay mineral/kerogen couplets (Calvert, 1966; Donegan and Schrader, 1981) also occur. The frequently intimate interbedding of clay and kerogen particles reflect their similar hydrodynamic properties, although distinct kerogen-rich and clay-rich couplets are also known (Gibling et al., 1985; Piasecki and Stemmarik, 1991).

The common occurrence of fine lamination in black shales has unfortunately led many authors to the erroneous conclusion that all shales (including black shales) are laminated (Curtis et al., 1980; Spears, 1980; Moon and Hurst, 1984; O'Brien and Slatt, 1990). Lamination, by definition, consists of very thin beds that have considerably greater lateral continuity than the constituent grains. A compacted fabric consisting of the parallel orientation of platy particles such as clay minerals and kerogen is not a true form of lamination (Fig. 2.2; Oschmann, 1988b, Fig. 8). All black shales show a compacted fabric but many are unlaminated (Wignall and Hallam, 1991). It is important that truly laminated black shales are distinguished from homogeneous varieties because the former imply episodic sedimentation and the latter more continuous accumulation.

There have been several schemes proposed for the classification of lamination types, mostly related to lateral persistence. In Grabowski and Pevear's (1985) study of the Green River Formation they distinguished 'continuous lamination' (laminae traceable across the width of a thin section) from 'discontinuous lamination' (laminae that only persist over a few centimetres are therefore seen to terminate within the width of a thin section). The latter category is equivalent to O'Brien and Slatt's (1990) lenticular lamination and is probably a common lamination type (Fig. 2.1). Nuhfer (1981) and Pye and Krinsley (1986) use the quantified index of percentage of continous lamination across the width of



Fig. 2.1. Photomicrograph showing couplets of coccolith laminae and slightly thicker clay mineral 'kerogen laminae. Opaque pyrite framboids are scattered throughout. The coccolith laminae are laterally impersistent (discontinuous lamination) and the couplets are of highly variable thickness ranging from 0.2 to 0.6 mm. Bed b19, mid-Pectinatus Zone. Upper Kimmeridge Clay, Freshwater Steps, Dorset.

the thin section to characterize lamination style. Grabowski and Pevear's third category 'internally orientated continuous lamination' or 'fabric lamination' of Lundegard and Samuels (1980) is the homogeneous fabric described above and is not a true form of lamination as it is not associated with compositional variations. Several authors have also documented a wavy lamination for laterally persistent laminae with undulatory contacts (Schieber, 1986: O'Brien, 1990; O'Brien and Slatt, 1990; Fig. 2.3); its origin is discussed below (Section 2.3).

#### 2.2 DEPOSITIONAL PROCESSES

#### 2.2.1 Hemipelagic settling

Most fine-grained terrigenous material is transported to basinal settings as aeolian dust and turbid nepheloid flows-very low density suspensions of sediment (Ewing and Thorndike, 1965; McCave, 1972). The settling rate from nepheloid flows is extremely low and the weak currents present in all seas and oceans would be sufficent to keep the material almost eternally in suspension (Pryor, 1975). Only the pyrite framboids formed within euxinic waters have sufficient density to fall rapidly to the sea bed (Dickman and Artuz, 1978). The majority of argillaceous material is removed from suspension by incorporation into faecal pellets or entrapment in gelatinous organic membranes (marine snow)—the former sink at 170 m/day and the latter at 95 m/day (Arthur *et al.*, 1984).

Faecal pellets, mostly derived from zooplankton, are particuarly good agents for the removal of both terrigenous and biogenic material from surface waters (Pryor, 1975; Porter and Robbins, 1981; Degens and Ittekkot, 1987). Dunbar and Berger (1981) observed that more than 120 000 pellets are produced per square metre per day in the Santa Barbara Basin and that pellets constitute between 60 and 90% of trapped settling material. Most faecal pellets are fragile and easily broken down but they are commonly preserved in low-energy black shale environments. In thin section the pellets occur as compacted, elongate lenses up to 2 mm in width although they are typically only 0.1-0.2mm in size (Hattin, 1981; Kemp, 1991; Dimberline et al., 1991; Fig. 2.4). Benthic worms such as capitellids can survive in suboxic conditions where they produce faecal pellets around 0.1 mm in size (Cuomo and Rhoads, 1987). The larger top-range sizes of zooplankton faecal pellets may help distinguish them from the pellets of such benthos. Dysaerobic fauna produce faecal pellets that are larger than zooplankton pellets (Porter and Robbins, 1981) although these may have a low preservational potential in bioturbated sediments.

Marine snow consists of amorphous, gelatinous



(a)



Fig. 2.2. (a) Thin section of an organic-rich shale from the Upper Kimmeridge Clay, Kimmeridge Bay (Bed 39c, Scitulus Zone). The homogenous fabric consists of parallel orientated platy particles of clay minerals and kerogen with scattered silt grains (fabric lamination). Field of view 1.8 mm high. (b) SEM image of the same specimen showing preferred particle orientation, occasional coccoliths lying parallel to the main fabric and centre left, a coccosphere. Field of view  $25 \,\mu$ m high.

organic particles, ranging from 0.5 mm to 10 cm in maximum dimension (Shanks and Trent, 1979). The snow may have multiple origins; algal-secreted mucopolysaccharides and faecal products of pelagic tunicates (sea squirts) have been suggested (Alldredge and Youngbluth, 1985; Degens and Ittekkot, 1987). A closely comparable product is the bacterially derived gelatinous particles documented from the density interfaces of hypersaline basins of the eastern Mediterranean (Erba *et al.*, 1987; Erba, 1991) which trap descending plankton.

The presence of sharp density contrasts, known as pycnoclines, in the water column is thought to be a

common feature of many black shale environments (cf. Chapter 6). The pycnoclines may exert an important control on hemipelagic settling as particles are frequently arrested in their descent and flocculent layers several metres thick may develop at this level (Mahoney, 1979). Eventually the concentration of particles reaches a sufficient density for the particles to break through and descend to the sea floor as a 'suspension storm' (Stanley, 1986; Niedermeyer and Lange, 1990). This produces fine laminae although the descent to the sea floor may be too rapid to permit efficient hydrodynamic sorting.

Hemipelagic sedimentation is characterized by zooplankton faecal pellets, fine lamination or a uniform preferred particle orientation, and an absence of evidence for erosion and winnowing (Fig. 2.5). On a basinal scale, pure hemipelagic settling deposits should form a blanket of strata of uniform thickness uninfluenced by regional variations in subsidence rates. That such 'blankets' are rarely observed for black shales, at least in epicontinental settings, testifies to an influence of bottom currents during black shale deposition.

#### 2.2.2 Turbidity currents

Low-density, low-velocity turbidity currents have been widely invoked as one of the principal depositional mechanisms for mudrocks, particularly for the common examples of finely interlaminated silt and mud (Piper. 1972, 1978; Hesse, 1975; Stow and Bowen, 1978; Stow and Shanmugam, 1980; Stanley and Maldonado, 1981; Pickering et al., 1986). Such turbidites are characterized by an upward gradation from silt-rich, mudpoor couplets to thinner silt-poor, mud-rich couplets. The exact process responsible for this discrete segregation of the silt and clav components of turbidity currents has been the subject of some debate. Piper (1972) proposed the alternation of silt deposition by tractional mechanisms and clay deposition by cohesion; multiple laminae occurring by fluctuations in clay concentration in the base of the flow.

Stow and Bowen (1978, 1980) noted that both clay and silt have similar critical settling velocities and that deposition of these components should therefore occur simultaneously. In order to achieve pulsed deposition, they proposed that clay floccules settling into the basal boundary layer of the turbidity flow are broken up by the increased shear stress at this level, and returned to suspension, allowing only silt to be deposited. Gradually the clay floccules increase in size until they reach the critical size necessary to settle through the boundary layer whereupon clay is deposited rapidly. The clay concentration in the base of the flow then decreases and silt-only deposition recommences and the whole pro-



Fig. 2.3. Thin section of the Permian Marl Slate from Quarrington Hill, County Durham showing wavy lamination defined by the undulatory contacts between the dark kerogen-rich laminae and the light carbonate/silt-rich laminae. Lamination is poorly developed and discontinuous in the upper half of the section. Field of view 2 mm high.



Fig. 2.4. Thin section of a very organic-rich shale showing a well developed parallel orientated fabric without lamination. The central elongate lens of coccolithic material is nearly 2 mm wide and may be an exceptionally large zooplankton faecal pellet. However, the bulk of the rock consists of organic-rich pellets or lenses generally less than 0.1 mm long. The Blackstone, Wheatleyensis Zone, Kimmeridge Clay, Clavell's Hard, Dorset.

cess is repeated. The model accounts for many features of the silt/clay couplets but not the usual presence of some clay within silt laminae. Therefore, Hesse and Chough (1980) propose that silt laminae are produced by multiple winnowing events, in a 'burst and sweep' model. The basal boundary layer is said to alternate between intervals of shear sorting, in which clay floccules are resuspended, and laminarized intervals during which clay accumulates by adhesion.

The distinct arrangement of silt/mud couplets, predicted by the above models, are not frequently seen in black shales; more common are isolated silt laminae persistent over centimetres but not metres (Dimberline *et al.*, 1990; Kemp, 1991). Such laminae could be deposited from low-density turbidity flows. In an absence of silt, pure mud turbidites can be recognized by the presence of sharp-based laminae, possibly showing small-scale load features and internal grading (Fig. 2.6).

Like hemipelagic settling, turbidity currents are also affected by the presence of density interfaces within the water column. If the stratification is intense or the turbidity current weak, a detached turbid layer results, in which the turbidity current flows along the top of the pycnocline dropping its load as a 'suspension cascade' (McCave, 1972; Stanley and Maldonado, 1981; O'Brien, 1989; Fig. 2.5). The product of such cascades is very similar to those of suspension storms (indeed the two processes are very similar) although grading is better 'developed by the particle-by-particle settling. Detached turbid layers spread their sediment over a much broader area than turbidity currents, producing a hemipelagic-like blanket of sedimentation. All other things being equal, the onset of stratification within a basin will therefore reduce sedimentation rates at any

### PROCESS

### PRODUCT

HEMIPELAGIC SETTLING	A A A A A A A A A A A A A A A A A A A	Compacted fabric of aggregates 0.1-2.0 mm in maximum width (zooplankton faecal pellets). Common pelagic fauna (ammonites, graptolites). "Blanket" stratigraphic distribution.	
SUSPENSION STORM		Poorly graded, laterally persistent, thin laminae.	
LOW DENSITY TURBIDITY CURRENTS		Couplets of silt and clay laminae showing an upward gradation to thinner, more clay-rich laminae. Individual silt laminae range from 0.5 - 10 mm thickness. In an absence of silt, graded mud laminae, possibly erosive-based occur.	ningen and some of the set of the
DETACHED TURBID LAYER SUSPENSION CASCADE		Thin, well sorted, graded laminae with sharp bases and tops. "Blanket" stratigraphic distribution.	euroscartantes cubilsett Méticanticalmentes Méticantes (* 1911)
CONTOURITES	X	Winnowed silt lenses and shallow erosional scours not filled with silt.	2/8:200000000000000000000000000000000000
STORM CURRENTS	>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>	High energy tempestites show erosive bases, rip-up clasts, allochthonous clasts and gutter casts. Lower energy examples consist of erosive-based, thin, graded laminae.	
INTERNAL WAVES		Winnowed lags and concentrations of pyrite/ phosphate clasts.	in the second and the

Fig. 2.5. Summary of depositional processes and products of fine-grained sedimentation.



Fig. 2.6. Graded mud laminae in a coccolith limestone (Freshwater Steps Stone Band, Upper Kimmeridge Clay). At the level of the coin very fine laminations of micrite and kerogen have been partly disrupted by *Zoophycus* burrows. At the base and top of the field of view the laminae are up to several centimetres thick, sharp and erosive-based and light to dark graded. The latter have been interpreted as the product of low-density turbidity currents triggered by storms (Wignall, 1989) whilst the thinner central laminae could be derived from supension cascades or other hemipelagic processes.

one site as the sediment is distributed over a much broader area (Stanley and Maldonado, 1981).

Major turbidity currents are able to penetrate density interfaces and temporarily oxygenate the bottom waters. In some instances this appears to allow animals that have survived transport in the turbidity current to thrive for a few weeks or months in an otherwise inhospitable environment (Sholkovitz and Soutar, 1975). Follmi and Grimm (1990) have aptly named such fauna 'doomed pioneers'.

#### 2.2.3 Bottom currents/contourites

Bottom currents are well known from modern deep oceanic settings where they constantly rework finegrained sediments and produce strata characterized by winnowed silt laminae and erosional scours (Piper, 1978; Fig. 2.5). Contourites are rarely recorded from black shales perhaps testifying to the rarity of benthic currents, although the common preferred orientation of palaeocurrent indicators suggests their presence, at least intermittently (Seilacher, 1982b).

#### 2.2.4 Storm currents

Storm-surge ebb currents are one of the principal mechanisms of sediment transport in epicontinental

seas (Aigner, 1985). It therefore seems likely that the many black shales known from such settings may have been influenced by storms. The presence of an allochthonous fauna in thin shell beds within black shales is commonly cited as evidence for storm sedimentation (Stel, 1975; Ayres et al., 1982) although the supposedly transported bivalves from the black shales of the Kimmeridge Clay (Aigner, 1980) are in fact autochthonous (Wignall, 1989; Oschmann 1990). Rarer evidence of storm processes in black shales includes gutter casts and lags of rip-up clasts produced by high-energy erosive events (Aigner, 1980; Wignall, 1989). More common products of storm activity consist of thin, erosive-based laminae deposited from storm-generated clouds of suspended material (Pedersen, 1985). Such beds may be difficult to distinguish from turbidites although the systematic grading of silt/mud couplets is not produced by storms (Fig. 2.5).

Many of the storm beds seen in black shales were probably produced by very infrequent. major storms. However, more minor, but much more frequent storms, may have been responsible for the brief oxygenation events and colonization episodes seen in many black shales (e.g. Sageman, 1989; Chapter 3). Such storms may have temporarily broken down water column stratification without causing major sea floor erosion.

#### 2.2.5 Internal waves

The presence of density interfaces, in a stratified water column, can produce internal waves at this level (Baird *et al.*, 1987; Thompson and Newton, 1987). At the intersection of the pycnocline and the sea floor, the impingement of the internal waves may lead to winnowing and erosion of the substrate, particularly on steeper palaeoslopes. Erosive-based lags of phosphate and pyrite nodules have been recorded (Baird *et al.*, 1987) but their most diagnostic feature is their occurrence around the rim of the black shale depositional area.

#### 2.3 BACTERIAL MATS

Bacterial mats are very common in modern suboxic settings where they exert a fundamental influence on sedimentation by trapping sediment and preventing sea floor erosion even under current velocities of up to 70 cm/s (Soutar *et al.*, 1981). Photosynthetic cyanobacteria (blue-green algae) such as *Oscillatoria* are found in benthic settings within the photic zone (Stewart and Pearson, 1970; Gallardo, 1977) but more common are mats of the non-photosynthetic, sulphur bacteria *Beggiatoa* and *Thioploca* which belong to the family of

gliding bacteria Beggiatoaceae. Their 'spongy' mats are widespread in modern oxygen-poor benthic environments at all water depths (Spies and Davis, 1979; Jørgensen, 1980; Soutar *et al.*, 1981; Juniper and Brinkhurst, 1986; Arntz *et al.*, 1991). They are generally encountered in suboxic environments where dissolved oxygen concentrations are between 0 and 0.2 ml/l although Arntz *et al.* (1991) record them at 0.2– 0.6 ml/l in the Peruvian upwelling system. The presence of grazers controls their upper oxygen range. As a result of this narrow range, bacterial mats often have a ringlike distribution around anoxic basins (Juniper and Brinkhurst, 1986).

The importance of the contribution of sulphur bacteria to the total sediment organic carbon budget is not fully evaluated. Juniper and Brinkhurst (1986) record fixation rates of 24 mg C/m<sup>3</sup>/day, although it is unclear if this is entirely autotrophic carbon production or if heterotrophism also contributes (Nelson and Castenholz, 1981). The Beggiatoaceae utilize hydrogen sulphide and other reducing substances to obtain energy for the dark fixation of carbon dioxide, but Arntz et al. (1991) note that they are partly heterotrophic as they are also able to incorporate a limited number of organic substrates. Nevertheless, the possibility remains that sulphur bacteria (and cyanobacteria) are major contributors to organic matter in sediments and thus to the genesis of hydrocarbon source rocks (Bauld, 1981; Williams, 1984; Williams and Reimers, 1983; Glikson and Taylor, 1985; Vercoutere et al., 1987).

Despite the ubiquity of bacterial mats on modern dysaerobic sediments it is very difficult to prove their former presence in ancient sediments. In fine-grained, lithographic-quality limestones radial crack patterns and reticulate ridges have been interpreted as cyanobacterial mats (Seilacher *et al.*, 1985) but such occurrences are exceptional. Bauld (1981) suggests that the common maceral alginite B may be derived from cyanobacteria. Evidence for sulphur bacteria is even more enigmatic. Williams and Reimers (1983) attribute scattered organic fibres, identified by SEM, to the mucilaginous sheaths of sulphur bacteria but they do not occur in anything approaching mat-like density. Biomarkers offer a possible means of identification, but none is forthcoming (Repeta *et al.*, 1992).

The wavy lamination often seen in thin sections of black shales (Fig. 2.3) has been considered as evidence for microbial mats (Schieber, 1986; O'Brien, 1990; O'Brien and Slatt, 1990) but this is unlikely for several reasons. It has not been demonstrated that *Beggiatoa*/ *Thioploca* mats are themselves wavy and, even if such microrelief is present, it is unlikely to survive compaction. Wavy lamination is probably produced by the differential compaction of organic matter around silt/ carbonate aggregates. Other authors have suggested that bacterial mats are associated with phosphatic cement (Williams and Reimers, 1983; Khan and Kelling, 1991) but this is rather an infrequent feature. Ultimately, the sheer abundance of sulphur bacteria in modern environments is probably the best evidence for their presence in the past.

#### 2.4 VARVES

Perhaps one of the most often repeated misconceptions of the black shale literature is the reported presence of varve couplets (or occasionally triplets) which can be used to calculate sedimentation rates. Varves are rhythmic alternations of laminae that record a years worth of deposition. Arthur et al. (1984, p. 532) state that, in black shales, 'Lamination represents preservation of the record of seasonal variation in supply of two or more components...' whilst Dimberline et al. (1991, p. 1147) similarly note, for silt laminae in black shales, that, 'a near-annual forcing mechanism is required to explain the periodicity of the silt input.' But why should this be so? In fact the rationale behind varve interpretations lies in the similarity of black shale 'varves' to the varves accumulating in several modern anoxic basins (Dickman, 1985). But, even in the modern sediments, many recent studies have shown that varves are rare (Stihler et al., 1992).

The fine coccolith-rich and kerogen-rich laminae forming in the Black Sea were thought to have formed as a result of a seasonally varying upper water column (Dickman and Artuz, 1978). Radiometric carbon-14 dating of the sediments has shown that the implied sedimentation rate of the varves is too high and that each 'varve' represents around three years of deposition (Calvert et al., 1991). This is a common problem with all supposed varves because their sedimentation rates are exceptionally high for hemipelagites. Varves must be greater than 0.1 mm in thickness as this is around the thickness of many of the constituent particles and they are difficult to discern at smaller thicknesses. This results in a compacted sedimentation rate of over 10 cm/1000 vrs-nearly an order of magnitude greater than values typical of hemipelagic deposition (Wetzel, 1982). In fact reported black shale varves are typically between 0.5 and 3 mm thick. In studies of black shales where a gross estimate of sedimentation rate is possible. 'varves' appear to represent between 3 and 20 years of deposition (Kemp, 1991). It is of course possible that varves do occur in black shales if the majority are

eroded-out by bottom currents. The general lack of erosive scours makes this unlikely. A more parsimonious explanation is that fine lamination couplets are the product of more episodic processes.

#### 2.5 BLACK SHALE SUBSTRATES

The nature of the substrate is an important factor in the palaeoenvironmental analysis of any sedimentary rock, not least because it exerts a strong control on the benthic fauna (Wignall, 1993a). Modern anaerobic sediments are extremely watery and soft (Bernhard, 1986). Sheu and Presley (1986, p. 105) describe surficial sediment from the anoxic Orca Basin as,



Fig. 2.7. Sharp junction, at the hammer head, between a blocky, fairly organic-poor mudstone and an overlying fissile, organic-rich shale. The close interbedding of such distinct weathering properties indicates that they are the product of differing depositional conditions rather than variations in the depth of burial (cf. White, 1961). Bed 39c of the Kimmeridge Clay (also seen in section in Fig. 2.2), Cuddle Cliff, Kimmeridge Bay, Dorset.

'extremely fluid-rich, with almost no shear strength' whilst Soutar and Crill (1977) describe Santa Barbara Basin sediments as 90% water—a precise sedimentwater interface is impossible to define in such conditions. The presence of these sediments testifies to the virtual absence of bottom currents. An unappreciated consequence of such soft sediment is that descending pelagic organisms, such as ammonites and marine reptile carcasses, may become instantly entombed within the sediment upon impact—a kind of 'autoburial' that may enhance their preservation (cf. Martill, 1987). Aigner's (1980) observation that vertically embedded ammonites are more abundant in black shales than in mudstones may be due to the ease with which ammonites sank into anaerobic muds.

The transition from anoxic to suboxic conditions is marked by a fundamental change to firm substrates due to the development of the bacterial mats, described above. Under increasing oxygen levels, grazers destroy



Fig. 2.8. Weathered outcrop of the Sulphur Band (immediately above the hammer) at Brackenberry Wyke. North Yorkshire illustrating the fissile weathering of this organic-rich (TOC = 8%), silt laminated shale.

the mats, and the development of a burrowing infauna can produce soft substrates, although other factors such as sedimentation rate and composition also influence substrate consistency (Wignall, 1993a).

#### 2.6 FISSILITY

Many black shales are characterized by their highly fissile weathering properties (Fig. 2.7) of which paper shales, with their thin, perfectly parallel sheets, are the best examples (Fig. 2.8). Ideas concerning the origin of this fissility have undergone considerable modification over the past few decades.

White (1961) demonstrated that fissility does not correlate with depth of burial and that it is therefore a depositional phenomenon. Meade (1966) went on to show that large amounts of organic matter and an initially high water content are prerequisites for good fissility-as noted in Section 2.5 both conditions are met during deposition beneath anoxic bottom waters. The presence of humic acids in organic-rich substrates disperses clay flocs thereby aiding the development of a preferred orientation of the clay mineral particles (Moon and Hurst, 1984) at pressures of as little as 1 kg/ cm<sup>2</sup> (Meade, 1966). Bioturbated mudrocks, on the other hand, have a homogeneous fabric of random clay particle orientations (Byers, 1974) and they are poorly fissile. In summary, fissility was considered to be the product of weathering of a compacted fabric of parallelaligned organic matter and clay particles accumulated beneath anoxic bottom waters.

More recent studies have challenged this view and suggested that fissility is a product of weathering of laminated rocks (Spears, 1976, 1980, 1981; Curtis et al., 1980; Archer and Hattin, 1984; O'Brien and Slatt, 1990). As laminae are preserved under anoxic bottom waters the genetic connotations of fissility are not altered but the underlying cause is. Spears (1976), in support of his case, demonstrated that lamination thickness is the same as shale fragment thickness in some Carboniferous black shales. However, this could simply be the product of weathering of shales with organic rich laminae (Lundegard and Samuels, 1981). It is the organic-richness not the laminae which is responsible for the fissility. I have encountered numerous examples of laminated, non-fissile mudrocks and fissile, unlaminated, but organic-rich shales. For example the shale in Fig. 2.7 is, by definition, fissile but in thin section it is unlaminated. The older viewpoint on the origin of fissility is supported by the greater bulk of geological data.

### 2.7 SYN-DEPOSITIONAL DEFORMATION

Black shales often show a surprising amount and variety of soft-sediment deformation particularly in finely laminated sediments where alternations of compositionally distinct material occur. Loop structures are amongst the most common features in which gaps, up to 1 cm wide, occur in continuous laminae by their symmetrical termination and constriction (Cole and



Fig. 2.9. Oil shale conglomerate in the White Stone Band, Upper Kimmeridge Clay, Brandy Bay, Dorset. Oil shale clasts, up to 50 cm in maximum dimension, float in a coccolith limestone matrix. Desiccation of oil shale is probably responsible for such layers, although overpressuring of only partly dewatered coccolith ooze may have aided the break-up of the shale. Picard, 1975; Grabowski and Pevear, 1985; Gibling *et al.*, 1985; Cater, 1987; Wignall, 1989). They are nearly always seen in more carbonate-rich laminae and represent subaqueous desiccation or synaeresis. Evidence of more substantial desiccation is provided by matrix-supported conglomerates (Fig. 2.9) and vertical fissures or 'mudcracks' (Bandel and Knitter, 1986; Wignall, 1989). Curiously such phenomena occur in organic-rich horizons in contrast to the carbonate loop structures. The presence of loops and mudcracks in the

Green River Formation oil shales of Utah and Wyoming was held as evidence for subaerial desiccation (e.g. Eugster and Surdam, 1973), but such features are also found in deep marine black shales (Wignall, 1989; cf. Section 8.3).

Recumbent shear folds, with their fold axes parallel to stratification are also seen in carbonate laminae (Grabowski and Pevear, 1985; Wignall, 1989). They may form by movement down the sides of transient gasescape mounds (Wignall, 1989).

# Palaeoecology

#### 3.1 THE RHOADS/MORSE/BYERS MODEL

The study of black shale palaeoecology was given great impetus with Rhoads and Morse's (1971) synthesis of the fauna of modern oxygen-deficient environments. Ironically, the main focus of their paper was on the explosive radiation of metazoans in the Cambrian rather than on black shales. They proposed that radiation was the result of dissolved oxygen levels in the world's oceans exceeding the threshold Pasteur point 0.1 ml/l, above which aerobic respiration was possible. However, they also introduced the concept of a dysaerobic zone (defined as dissolved oxygen levels between 0.1 and 1.0 ml/l—see Fig. 3.1(a)) which could be recognized by its distinct faunal and sedimentological character.

The transition from the aerobic to the dysaerobic zone is marked by the loss of the majority of shelly taxa. Soft-bodied polychaetes and nematodes are dominant although crustaceans and echinoderms generally remain common. In the Gulf of California dysaerobic zone protobranch bivalves and the thick-shelled gastropod Nassarius also occur (Parker, 1964). Rhoads and Morse (1971) attributed the rarity of shelly taxa to the difficulties of calcium carbonate secretion under high pCO<sub>2</sub> and lowered pH values commonly encountered in low oxygen settings. Deposit feeding is the commonest life strategy amongst the dysaerobic fauna and their active burrowing destroys all sedimentary structures. However, in the lowest realms of the dysaerobic zone, between 0.1 and 0.3 ml/l, metazoan activity becomes severely reduced and tiny nematodes remain the only actively burrowing fauna, but these are too small to disrupt lamination. Whilst no macrofauna can survive in the anaerobic zone, some foraminiferans appear able to survive in the upper reaches of this zone with levels of dissolved oxygen between 0 and 0.1 ml/l.

The validity of Rhoads and Morse's model to the study of ancient black shale faunas was subsequently demonstrated by Byers (1977), and the model is now known as the Rhoads/Morse/Byers (RMB) model. Byers used dysaerobic both as an environmental term (Rhoads and Morse's original usage) and as a biofacies defined as 'calcareous epifauna lacking, but sediment bioturbate due to the activities of [oxygen] resistant fauna.' (Byers, 1977, p.6). This rather over-simplified the situation for, as Rhoads and Morse had noted, calcareous epifauna can be present and the lowest reaches of the dysaerobic biofacies are laminated not bioturbated. Subsequent studies of modern dysaerobc faunas along the western seaboard of North America have added further detail to the RMB model and somewhat modified its diagnostic details.

In their study of the biofacies in several basins of the California Continental Borderland, Savrda *et al.* (1984) noted that there is a rather gradual decline in species richness across the aerobic/dysaerobic boundary and that shelly taxa such as ophiuroids, crabs, and the gastropod *Mitrella* thrive in the lowest dysaerobic biofacies. Savrda and his co-workers also considered that any lamination in dysaerobic biofacies is due to incursions of anaerobic biofacies (Fig. 3.1(b)) rather than a product of conditions unique to dissolved oxygen concentrations of 0.1–0.3 ml/l. Theirs was also the first study to use anaerobic/dysaerobic/aerobic in a purely biofacies sense—a usage followed here.

The dysaerobic fauna associated with the central Californian oxygen minimum zone (OMZ) also departs somewhat from the RMB model predictions. Echinoderms (asteroids, ophiuroids, echinoids) appear to be particularly abundant in this setting (Thompson et al., 1985; Vercoutere et al., 1987) and a moderately diverse calcareous fauna is found until oxygen concentrations drop below 0.3 ml/l. Thompson et al. (1985) therefore recommended that levels between 0.1 and 0.3 ml/l should define dysaerobic biofacies. This is rather restrictive and fails to account for the oxygenrestricted nature of the fauna above 0.3 ml/l. However, the proposal of Thompson et al. once again recognizes that the lowest dysaerobic biofacies, as originally described by Rhoads and Morse (Fig. 3.1(a)), is characterized by sedimentary and faunal characteristics distinct from upper dysaerobic biofacies (contrary to the views of Savrda et al., (1984)). The term quasianaerobic is available to describe this biofacies (Tyson and Pearson, 1991). The highly diverse dysaerobic fauna of the Californian OMZ may be attributable to the longterm stability of this environment, on a scale of decades (Churgin and Halminski, 1974; Vercoutere et al., 1987), allowing specialist dysaerobic taxa to become established (Wignall, 1990b).



Fig. 3.1. Developments of the Rhoads-Morse-Byers model for oxygen-restricted faunas. (a) The model as originally proposed by Rhoads and Morse (1971) with only a few shelly taxa in the dysaerobic biofacies and laminated sediments in lowest oxygen and anoxic conditions. (b) The model as modifed by Savrda *et al.* (1984) with dysaerobic sediments entirely bioturbated. (c) New terminology of Rhoads *et al.* (1991). 1, Shelly taxa; 2, soft-bodied taxa.

Rhoads *et al.* (1991) considerably modified the terminology of the RMB model (Fig. 3.1(c)). In particular, they acknowledged the observation of Savrda *et al.* (1984) that there is no sharp faunal change between the dysaerobic and aerobic biofacies and they propose a transition zone between these two categories. Apart from mixing a 'zone' with 'biofacies', in practice this new scheme has the disadvantage of how to define *two* boundaries whereas before there was only the problem of defining one. When assessing palaeo-oxygen gradients, the aerobic/dysaerobic boundary should be taken at the level where the first influence of oxygen-restrictive conditions can be detected (see Section 3.5).

The RMB model, as it currently stands, offers the following paradigms for detecting a declining oxygen gradient in the geological record:

(1) A decline in benthic species diversity, dropping to zero at the anaerobic/dysaerobic boundary.

(2) A decline in the size of the benthos. This is particularly reflected in the maximum burrow diameter.

(3) A transition from burrowed to laminated sediment. In the RMB model this occurs low in the dysaerobic biofacies whilst Savrda *et al.* (1984) consider that it occurs at the anaerobic/dysaerobic boundary. The extensive occurrence of bacterial mats in unbioturbated lowest-dysaerobic sediments in many modern suboxic settings (see Section 2.3) may be the source of lamination in lowest dysaerobic sediments.

(4) A change in the life strategies of the benthos. Deposit feeders become dominant, whilst suspension feeders are rare (Edwards, 1985). Active, mobile forms, particularly carnivores, are inhibited by low oxygen levels (Douglas, 1981).

(5) The loss of many shelly taxa, although many echinoderms, protobranch bivalves, and some gastropods can thrive in dysaerobic biofacies. Due to the difficulties of calcium carbonate secretion, poorly ornamented shelly taxa will be dominant.

The RMB model and its modifications is mainly derived from observations of natural oxygen-poor environments, the majority of which have remained stable for decades and frequently centuries. In those instances where dissolved oxygen levels have undergone short-term fluctuations, the benthic fauna is considerably different from that encountered during stable conditions. An oxygenation event in the last century (around 1840) in the normally anoxic Santa Barbara Basin allowed the colonization of the tellinid bivalve Macoma leptonides (Soutar and Crill, 1977; Schimmelmann et al., 1992). Similarly, a brief improvement in benthic oxygen levels on the Guayamas Slope, in July 1978, saw the appearance of 'small pectens (up to 100 per square meter)' (Soutar et al., 1981, p. 143). Dynamic dysoxic environments are more commonly encountered in shelf seas. The relevance of these environments to black shale studies is assessed below.

# 3.2 DYSAEROBIC FAUNAS OF MODERN SHELVES

Oxygen-deficient environments are frequently encountered in many modern shelf seas, particularly in temperate latitudes where a summer thermocline develops (Tyson and Pearson, 1991). In many cases the high oxygen demand of man-made pollution, particularly sewage, intensifies the oxygen deficiency and low dysoxic or even anoxic conditions may occur locally with catastrophic results for benthic populations (e.g. Boesch and Rabalais, 1991; Stachowitsch, 1991). The effects on the fauna have been documented in detail; there are many parallels with the RMB model.

Under declining bottom-water oxygen levels, there is a progressive loss of benthic species until all disappear around 0.3-0.5 ml/l (Tyson and Pearson, 1991), although the precise dissolved oxygen value is highly variable and depends on several factors (see below). In the absence of a benthos, sulphur bacteria mats coat the sediment until truly anoxic conditions are established. Some polychaete and bivalve species are amongst the last to be lost from the benthic assemblages. The tiny polychaete Capitella capitata is commonly characteristic of the most impoverished assemblages although this 'species' may represent several sibling species (Pearson and Rosenberg, 1978). Several bivalves can also withstand low dysoxic conditions, particularly Macoma balthica, Arctica islandica, Corbula spp., and Astarte spp. (Pearson, 1975; Taylor and Brand, 1975; Pearson and Rosenberg, 1978). Bivalves and many other invertebrate groups have the ability to switch to anaerobic metabolic pathways for short periods. This is particularly so for mud-dwelling taxa and intertidal taxa which commonly encounter anoxic conditions. Such facultative anaerobiosis is generally achieved by using stored carbohydrates. Bivalves commonly use the glucose-succinate pathway (Hochachka and Mustafa, 1972; de Zwaan, 1977; Livingstone, 1983).

In sediments accumulating beneath a normally oxygenated water column there is a sharp boundary between reduced and overlying oxygenated sediment. called the redox potential discontinuity or RPD zone, which is controlled by the depth to which infauna can bioturbate and irrigate their burrows. As bottom-water oxygen levels decline, infauna are progressively less able to pump oxygen into the sediment with the result that the RPD zone rises and infaunal organisms are driven out onto the sediment surface (Ankar and Jansson, 1973; Rosenberg, 1977 Ropes et al., 1979; Stachowitz, 1991). After evacuation, the final act of many dving bivalves is to extend their siphons as far as possible above the sea floor for normally oxygenated waters may be quite close to the bottom. For example, Arntz and Rumohr (1986) recorded a change from anoxic water at the sediment surface to normal oxygen values only 40 cm above the surface, whilst Rosenberg (1977) recorded a similar sharp gradient within 1 m of the sea floor.

The low oxygen levels necessary to eliminate all benthic metazoa vary depending on the temperature, salinity, presence of hydrogen sulphide, and the rate of decline of oxygen values. Thurberg and Goodlett (1979) showed that bivalves could survive much better at dissolved oxygen concentrations of 0.7ml/l if they were gradually acclimatized to such levels rather than being suddenly introduced to them. The rapid transition to dissolved oxygen values of 1.0 ml/l in the German Bight in 1982 was sufficient to kill many fish, ophiuroids, and bivalves (Dethlefsen and von Westernhagen, 1983), even though such values have a minimal effect in more stable environments. In many dysoxic situations it is clear that the actual cause of death is due to poisoning by hydrogen sulphide rather than suffocation due to lack of oxygen; juvenile forms appear to be particularly susceptible to the effects of hydrogen sulphide (Theede *et al.*, 1969; Steimle and Sindermann, 1978).

Benthos are generally even less able to survive under the combined effects of low oxygen levels and lowered salinity (Bayne, 1973), probably because of an increased oxygen uptake as more energy is needed for osmoregulatory processes (Shumway, 1982). The interdependence of oxygen and temperature is less easily determined. The solubility of oxygen declines with increasing temperature, implying that warmerwater faunas are generally more likely to encounter dysoxic conditions and that they should therefore be more tolerant of such conditions. In fact the opposite is observed, for high-latitude, particularly Arctic, benthos are more tolerant of a range of oxygen values (Theede et al., 1969; von Oertzen and Schlungbaum, 1972; Webster, 1975; Rosenberg, 1977). The reasons for this pattern are unclear although Theede (1973) has suggested that anaerobiosis may be easier in colder water.

It is difficult to ascertain a ranking of oxygen tolerance amongst benthic organisms, particularly at the species level, because the degree of intraspecific variability is often far greater than at the interspecific level (Mackay and Shumway, 1980; Herreid, 1980). Mangum and van Winckle (1973, p. 529) despairingly noted that, 'the distribution of the response to declining oxygen levels appears to defy comprehension.' An individual's oxygen tolerance is dependent on a complex, linked array of factors, including temperature, salinity, its size, and above all the general health of the animal (Herreid, 1980).

The relationship between organism size and oxygen tolerance is also complex. In general, a declining oxygen gradient causes the progressive elimination of the larger soft-bodied taxa until only small infaunal polychates, oligochaetes, and nematodes survive (Pearson and Rosenberg, 1978; Pearson et al., 1985; Tyson and Pearson, 1991). The size of burrows thus declines, as proposed in the RMB model. Undoubtedly a size decrease is advantageous for organisms which respire across their skin due to the higher surface area to volume ratio of smaller organisms. However, for organisms, such as bivalves, with more sophisticated respiratory systems involving gills, adults appear more tolerant of dysoxia (Bayne, 1971; Taylor and Brand, 1975; Leppakoski, 1975; Lane and Lawrence, 1979; Thurberg and Goodlett, 1979). Adults may be generally more hardy than juveniles, although the increased metabolic rate of rapidly growing juveniles is probably disadvantageous in low-oxygen settings (Zeuthen, 1953). Many low-oxygen settings are therefore characterized by populations of adult bivalves with no juveniles, producing a distinctive size-frequency curve (Leppakoski, 1975; Andersin *et al.*, 1978). In many cases, the juvenile forms may be absent due to their intolerance of hydrogen sulphide rather than an inability to cope with low oxygen values (Tyson and Pearson, 1991). Like many so-called faunal 'trends' in dysoxic shelf settings there are numerous exceptions. Thus Shumway *et al.* (1983) could find no oxygen/size relationship in the coot clam *Mulina lateralis* except at water temperatures of 20 °C when smaller individuals were found to be more tolerant of anoxia.

In the RMB model, a declining oxygen gradient favours deposit feeding and grazing trophic groups at the expense of suspension feeders and carnivores; active, mobile forms are notably absent. A similar pattern occurs amongst soft-bodied taxa in shelf settings but shelly taxa exhibit more complex trends. Thus, the common dysoxic bivalve Macoma balthica is a non-selective deposit feeder that can also supplement its diet by filter feeding (Brafield and Newell, 1961; Tunnicliffe and Risk, 1977), whilst the majority of bivalves from shelf dysoxic settings are filter feeders (Pearson et al., 1985; Rosenberg, 1976). Under the lowest oxygen levels there may be a peak of carnivores which exploit an over-abundance of prey, particularly infaunal forms driven onto the surface by a rising RPD zone (Pearson and Rosenberg, 1978). The presence of suspension feeders and carnivores is not predicted by the RMB model.

Changes in epifaunal/infaunal ratios under declining oxygen levels are highly variable. Dysoxic conditions are more frequently encountered in infaunal life sites, and infaunal species are commonly more euryoxic than epifaunal species living in the same environment (Theede, 1973), implying that infauna should become dominant. However, deep infaunal life sites are a nongst the first to become uninhabitable as oxygen levels decline and highly euryoxic epifaunal communities also occur (Tunnicliffe, 1981).

The numerous differences between the predictions of the RMB model and the trends observed in shelf settings probably relate to the much greater temporal variability of the latter. Instability favours opportunistic forms in which high reproductive rates, rapid growth, short life spans, and a planktotrophic larval stage are important. Thus the common lowest dysoxic species *Capitella capitata* and *Macoma balthica* do not appear to be particularly tolerant of low oxygen levels (Pearson and Rosenberg, 1978; Shumway *et al.*, 1983) but they

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are both classic opportunists able to rapidly colonize an area within a few weeks or months. Thus, it is rarely possible to predict the taxa in the most impoverished assemblages using ranked species lists of oxygen tolerance alone (e.g. Dries and Theede, 1974) as such lists do not take into account the opportunism of the faunas. The most rapid colonization can be achieved by adults of highly mobile taxa, such as crustacea or ophiuroids, which are able to migrate into an area as soon as harmful conditions have ceased. Such adult-migration events may be particularly important if the original inhospitable area was small.

Suspension-feeding taxa are generally more opportunistic than deposit feeders because they exploit a food resource (plankton blooms) that is more unpredictable than the sediment eaten by deposit feeders. The preferential success of suspension-feeding bivalves in dysoxic settings is probably due to this factor. A dysoxic faunal gradient in shelf settings is recording not so much the oxygen levels as the duration of habitable conditions. Lowest dysoxic conditions allow only very brief benthic colonization events, of perhaps a few months only. Normal benthic communities require between five and eight years of normal conditions in order to become established (Rosenberg, 1976; Leppakoski, 1975).

An alternative shelf model for oxygen/stabilitycontrolled faunal gradients, based on shelf faunas, is given in Fig. 3.2. Anaerobic sediments are produced under conditions where bottom-water oxygen levels remain permanently below 0.5 ml/l. Bacterial mats may thrive if bottom waters do not become sulphidic and the sediments are typically laminated. Lowest dysaerobic sediments are also laminated but they contain speciespoor shell pavements and microbioturbation horizons representing transient colonization events (an example is recorded by Schimmelmann et al. (1992) from the normally stable Santa Barbara Basin). Such events probably last for less than a year because more prolonged benthic faunal activity results in the destruction of fine lamination (e.g. Soutar et al., 1981). Suspensionfeeding bivalves and mobile forms, such as ophiuroids, are typical faunal elements. In upper dysaerobic biofacies the increasing duration of oxygenation events allows a greater diversity of benthos to become established and greater irrigation of the sediment causes the RPD zone to become deeper with the corresponding



Fig. 3.2. New model for oxygenrestricted faunas based on the dynamically unstable dysoxic environments of some modern shelf seas. disruption of lamination. The aerobic/dysaerobic divide can be taken at the appearance of deep infaunal forms which are normally highly susceptible to lowered oxygen levels.

Under a declining dysoxic gradient, the shelf model predicts:

(1) A decline in benthic species richness to zero at the anaerobic/dysaerobic boundary.

(2) A general decline in the size of organisms, particularly soft-bodied taxa. Larger bivalves are generally more tolerant of low-oxygen conditions.

(3) A decrease in the depth and size of burrows until, in the lowest dysaerobic biofacies, burrows are too small to disrupt millimetre-scale lamination.

(4) There is no general trend in life strategies or life sites. Opportunistic species become more common and, for bivalves, these tend to be suspension-feeding forms but many opportunistic polychaetes are deposit feeders. There is no clearly distinguishable trend in infaunal/epifaunal ratios either; only deep infaunal forms are absent from dysaerobic sediments.

(5) There is no clear change in the relative proportions of soft-bodied to shelly taxa.

Only predictions (1) and (3) are in accord with the RMB model. The dysaerobic biofacies as defined here is, however, similar to the poikiloaerobic biofacies of Oschmann (1991). The use of the term poikiloaerobic rather than dysaerobic is preferred as it helps to distinguish the shelf model predictions from those of the RMB model, although this requires some redefinition of Oschmann's original usage.

Oschmann (1991, p. 391) defines his poikiloaerobic biofacies as forming in conditions in which annual anoxia does not persist for more than three months per year. In fact oxygen does not have to be totally absent, dissolved oxygen levels of less than 0.5 ml/l are sufficent for all benthic forms to disappear (Tyson and Pearson, 1991). Oschmann considered the poikiloaerobic macrofauna to consist of rare soft-bodied and shelly fauna. The use of 'rare' is misleading for shells can be extremely common on certain horizons (e.g. Schimmelmann et al., 1992) and the soft-bodied meiofauna is prolific in lowest dysaerobic sediments (Tyson and Pearson, 1991). Species-poor rather than rare is a more apt description of poikiloaerobic faunas. Oschmann also considers poikiloaerobic faunas to be dominantly infaunal suspension feeders but, as discussed above, neither life sites nor feeding strategies are useful predictors of oxygen/stability gradients.

With the above modifications, poikiloaerobic is a useful term for the description of black shale faunas. A lower/upper poikiloaerobic divide is also added in Fig.

3.2 at the boundary between laminated and burrow-mottled strata.

#### 3.3 CHEMOSYMBIOSIS—A PANACEA FOR BLACK SHALE FAUNAS?

Our knowledge of invertebrate feeding strategies has undergone a revolution over the past two decades with the discovery of bacterial symbiosis in polychaetes, oligochaetes, nematodes, and molluscs (Vetter et al., 1991). This diverse range of taxa derive their nutrients from the farming of hydrogen sulphide-oxidizing or methane-oxidizing bacteria in their gill tissues and consuming by-products such as ribulosebisphosphate carboxylase (Southward, 1986). As hydrogen sulphide is highly toxic for most invertebrates (Theede et al., 1969), chemosymbionts have active systems of detoxification that require an ample oxygen supply (Reid and Brand, 1986; Vetter et al., 1991). Hydrogen sulphide and methane are rapidly oxidized in the presence of oxygen, therefore chemosymbiosis is encountered in a very distinct range of environments characterized by sharp redox boundaries.

The most diverse chemosymbiotic communities are associated with hydrothermal vents on spreading ridges where hot sulphide-rich solutions provide a source of hydrogen sulphide in well-oxygenated abyssal environments. Giant pogonophoran tube worms and the large mytilid bivalve Calyptogena dominate such communities whilst polychaetes, archaeogastropods, and crabs are minor elements (Hand and Somero, 1983; Turner and Lutz, 1984). Hydrothermal vents are widely distributed throughout the oceans but their associated faunas are usually very similar. 'Stepping stones' for the dispersal of vent faunas appear to be provided by decaying whale carcasses which provide a local supply of hydrogen sulphide (Smith et al., 1989). Squires et al. (1991) report Mytilus and lucinids associated with Oligocene whales, suggesting that similar dispersal mechanisms operated in the past.

In passive margin settings, syn-depositional faulting can allow the escape of hydrocarbons, particularly methane, at the sea floor. The associated faunas of 'cold seeps' include pogonophorans once again, and mytilids such as *Calyptogena soyoae* with methanotrophic symbiotic bacteria (Cary *et al.*, 1988; Hashimoto *et al.*, 1989). The intense bacterial oxidation of methane at the sea floor can produce extensive carbonate cementation in the form of gentle mounds or 'pseudobioherms' up to 60 m in diameter. The associated faunas of such mounds are amongst the most reactily identified chemosymbiotic communities in the fossil record (Gaillard and Rolin, 1986; Beauchamp *et al.*, 1989). Although modern cold seeps occur in fully oxygenated marine settings several ancient examples are found within black shales where sulphide-oxidizing symbioses may have been important (Howe *et al.*, 1987; Rolin *et al.*, 1990). The black shale examples also differ in having a fauna dominated by lucinids rather than mytilids.

Bacterial gill symbiosis appears to have arisen several times amongst the Bivalvia for it is encountered in protobranch, filibranch, and lamellibranch gills (Southward, 1986). The Lucinidae and Thyasiridae families of the Lucinacea superfamily comprise one of the largest and most successful chemosymbiotic bivalve groups (Reid and Brand, 1986). In the past they are found amongst cold seep assemblages but in the present day they are encountered amongst the roots of seagrasses where abundant decomposing vegetation produces hydrogen sulphide concentrations up to 4 millimoles (Vetter et al., 1991). Oxygen is also available as it is released by the roots of the seagrass (Fisher and Hand, 1984). As a consequence of this ready availability of oxygen, the infaunal lucinaceans do not construct an inhalent tube, although they produce a complex, interconnected burrow system beneath their shell to tap hydrogen sulphide from the deeper sediment (Dando and Southward, 1986).

The unusual solemyid bivalves appear to be the only chemosymbionts able to cope with dysoxic conditions whilst pursuing this life-style, for they are encountered in sewage-polluted environments (Reid and Bernard, 1980; Felbeck, 1983). Despite the general rarity of chemosymbionts in modern dysaerobic sediments, several authors have suggested that it may have been an important, if not dominant, mode of life for many ancient black shale faunas (Savrda and Bottjer, 1987b; Kauffman, 1988; Seilacher, 1990; Savrda *et al.*, 1991). Proving such assertions is fraught with difficulties.

Chemoautotrophic bivalves are characterized by light carbon isotopic ratios but, unfortunately for palaeoecologists, the ratios in their preservable hardparts are more variable (Dando and Southward, 1986). *Calyptogena magnifica* from hydrothermal vents has very light  $\delta^{13}$ C values (Rio *et al.*, 1988) whilst Macleod and Hoppe (1992) reported heavy values from coldseep faunas. Macleod and Hoppe (1992) further recorded heavy isotopes from inoceramids (common constituents of many Jurassic-Cretaceous black shale faunas) which they suggest indicates a chemosymbiotic lifestyle, although Grossman (1993) considers this unlikely.

Seilacher (1990) suggested that burrows constructed by the Lucinacea closely resemble the common lower dysaerobic trace fossil *Chondrites*. However, I am not aware of a single reported co-occurrence of these fossils. Seilacher (1990, Fig. 3) also misrepresents Dando and Southward's (1986) original figure of *Thyasira* burrows because their interconnected galleries only superficially resemble the repeatedly branching burrows of *Chondrites*.

In fact there are several lines of evidence that suggest that chemosymbiosis was not important in black shale faunas. For example:

(1) Fossil occurrences of known chemosymbionts, such as the lucinaceans and solemyids, are rarely, if ever, encountered in lower dysaerobic strata (Wignall, 1990a; Nobuhara and Tanaka, 1993), except in the case of cold seep carbonate mounds where the chemosymbiotic fauna (normally lucinaceans) is different from the interbedded black shale faunas (Rolin *et al.*, 1990).

(2) Chemosymbionts utilize a stable food resource and so, like deposit feeders, they tend to be specialists with poor dispersal rates unsuited to unstable environments. Many black shale environments are highly dynamic (Sageman, 1989; Sageman *et al.*, 1991) rendering them difficult for chemosymbiont colonization.

(3) Modern chemosymbiotic bivalves are, without exception, infaunal whilst the majority of black shale bivalves are epifaunal (see Section 3.8).

(4) Chemosymbiosis requires ample supplies of oxygen and consequently this life strategy is rarely encountered in dysoxic environments, with the notable exception of the solemyids.

Chemosymbiosis has arisen several times in unrelated invertebrate groups and it is of course possible that extinct black shale faunas may have developed this life strategy, but the available evidence from the modern fauna suggests that this is highly unlikely.

#### 3.3.1 Thiobios

Several years before the discovery of the chemosymbiotic life strategies. Fenchel and Riedl (1970) had noted that some small invertebrates occur as much as 50 cm beneath the sediment surface, deep within anaerobic sediments. Most of this fauna belongs to softbodied meiofaunal groups such as gnathostomulids, turbellarids, nematodes, and gastrotichs. Fenchel and Riedl named this the sulphide biome whilst Boaden and Platt (1971) renamed it the thiobios. Fenchel and Riedl considered that the thiobios may be obligate anaerobes, fixing carbon dioxide during respiration and feeding on bacteria. Their type examples were recorded from intertidal beach sands but obligate anaerobes should also theoretically thrive in anaerobic muds. In fact no thiobios has ever been recorded from an anoxic depositional environment.

The thiobios appears to utilize facultative anaerobiosis and is tolerant of hydrogen sulphide, but it still requires oxygen (Maguire and Boaden, 1975; Vetter *et al.*, 1991). Reise and Ax (1979) suggested that the concept of a thiobios was unnecessary because Fenchel and Reidl (1970) had failed to appreciate the heterogeneity of sediments and the ability of macrofauna to irrigate sediments to a depth of 50 cm. The majority of so-called thiobios in fact live in burrow walls where there is a high bacterial density (Reise and Ax, 1979).

The thiobios concept was resurrected in highly modified form by Powell et al. (1983) in their study of a meiofauna associated with a sharp redox boundary. They defined such fauna, which is taxonomically similar to the assemblage listed above, as having a requirement for sulphide whilst still remaining obligate aerobes. This is a considerable departure from Fenchel and Riedl's original definition and rather confuses the issue, because the chemosymbiotic macrofauna discussed above now fall into this definition but these have high oxygen requirements whilst meiofaunal thiobios by any definition are euryoxic. Considerable further research is required on the mode of life of the meiofaunal thiobios. For example, thiobiotic nematodes tend to be longer and thinner than their normal relatives, possibly as an aid to absorption of dissolved organic matter (Nicholas, 1991).

The meiofauna encountered in the laminated, lower dysaerobic biofacies of the RMB model could belong to the thiobios (*sensu* Powell *et al.* 1983). Oschmann (1988a) has claimed the presence of an obligate anaerobic thiobios (*sensu* Fenchel and Riedl) in Kimmeridge Clay black shales but, as discussed above, such a fauna does not exist (Reise and Ax, 1979).

#### 3.4 DYSAEROBIC BENTHIC FORAMINIFERA

Like all benthic taxa, the relative fortunes of foraminiferans under a declining oxygen gradient can be used as a valuable palacoecological index. Foraminiferans decline in diversity as benthic oxygen levels decrease, although in modern environments at least, they appear relatively less affected than other benthos and so become proportionately more important. Thus, the upper anaerobic sediments of the RMB model can contain foraminiferans which may be present in abundance due to the absence of their usual predators (Douglas, 1981). Koutsoukos *et al.* (1990) coined the term quasi-anaerobic for this biofacies to distinguish it from the truly metazoan-free anaerobic biofacies (cf. Fig. 1.1). Whilst it is valid to define a readily determined subdivision of the original model, quasi-anaerobic biofacies are rather time specific. Laminated sediments containing only foraminiferans are known from the Cretaceous to Recent, but prior to this foraminiferans do not appear to have been any more oxygen tolerant than other groups such as bivalves (Wignall, 1990c). Occurrences of species of *Bolivina*, which appeared in the Cretaceous, and the Tertiary to Recent *Bulimina* define most reported quasi-anaerobic biofacies.

Due to the difficulties of calcium carbonate secretion in low-oxygen environments, dysaerobic foraminiferans tend to be thin-shelled and poorly ornamented (Harman, 1964; Govean and Garrison, 1981; Douglas, 1981; Bernhard, 1986). For this reason agglutinating foraminiferans are proportionately more common amongst dysaerobic than aerobic assemblages (Koutsoukos et al., 1990). Broad flat forms should theoretically also be favoured in low-oxygen settings due to their relatively greater surface area for respiration. This is commonly observed (e.g. Koutsoukos et al., 1990) although Bernhard's (1986) compilation of dysaerobic morphotypes is most notable for the great range of forms including cylindrical morphologies which are clearly not optimizing their surface area. Small size is another often reported feature of dysaerobic foraminiferan populations, held to indicate the early onset of reproductive maturity in opportunistic taxa (Govean and Garrison, 1981).

An ability to rapidly colonize transiently favourable environments is probably the most important factor for black shale foraminiferans and benthic taxa in general (Section 3.2). In many instances the degree of 'opportunism' may transcend any supposed oxygen-related trends. For example, van der Zwaan and Jorissen (1991) could find no infaunal/epifaunal trends in their survey of foraminiferans from recent oxygen-restricted environments. The failure to find a morphology specific to dysoxic conditions is probably because of the overriding importance of recruitment rates. Species richness and also perhaps agglutinating calcareous ratios may be the best measure of palaeo-oxygen gradients.

#### 3.5 DYSAEROBIC TRACE FOSSILS

Trace fossils are a valuable source of data in black shale analyses. The destruction of a preferred fabric orientation by burrowing is an important marker within both the RMB and shelf models (Figs. 3.1 and 3.2). More sophisticated schemes have also been devised.

Under normal oxygen regimes a complex, tiered burrow system is developed (Fig. 3.3). The deepest

burrowers routinely excavate anaerobic sediments but they are able to survive by irrigating their burrows and mucus-lining their walls (Wetzel, 1991). Under a declining oxygen gradient it becomes progressively more difficult to oxygenate within the sediment and the deepest tiers become shallower whilst the shallower tiers are lost. There is also an associated decline in diversity and decrease in the mean burrow diameter reflecting the decreasing size of the organisms predicted in the RMB model (e.g. Jordan, 1985; Savrda and Bottjer 1986, 1987a; Leszczynski, 1991).

By utilizing the changing tiering patterns, Savrda and Bottjer (1986, 1987a) have reconstructed the temporal variability of oxygenation and deoxygenation events. Under conditions of gradually declining oxygen there is a gradual upward loss of ichnogenera and a simplification of cross-cutting relationships (Fig. 3.4(a)). Such events must occur over periods of thousands of years for there to be sufficient mudrock accumulation to preserve the trace fossil relationships. High-frequency fluctuations, such as those implied by poikiloaerobic biofacies, simply 'freeze' tiered profiles (Fig. 3.4(b)).

There have also been many attempts to define palaeo-oxygen gradients using specific ichnogenera but, with the exception of *Chondrites*, there is little consistency between the studies (Fig. 3.5) and they are clearly of little predictive use. *Chondrites* is a branching, root-like fodinichnial trace which is widely held as an indicator of lowest-oxygen conditions when it is the sole trace fossil encountered (Bromley and Ekdale, 1984). But even Chondrites fails to occur in the predicted place in many British Jurassic black shales; for example, in the Kimmeridge Clay it is restricted to upper dysaerobic mudstones (Wignall, 1991b; Fig. 3.5) whilst lowest diversity trace fossil assemblages consist of the small pasichnial trace Astacimorphichnus (Fig. 3.6). Much of the discrepancy between the Kimmeridge Clay trace fossils and the type examples of Savrda and Bottjer's and Bromley and Ekdale's schemes may lie in the distinction between dysaerobic and poikiloaerobic biofacies and the degree of environmental stability. Wetzel (1991) suggests that Chondrites trace makers can only develop under long-term low-oxygen conditions. Chondrites may therefore be an indicator of lower dysaerobic but not lower poikiloaerobic biofacies. The Astacimorphichnus horizons from the Kimmeridge Clay show evidence for the highly transient nature of benthic colonization (Fig. 3.7). On any one bedding plane all specimens tend to be the same length, implying single-cohort colonization by meiofaunal-sized organisms such as nematodes.

Ekdale and Mason (1988) have also used the behavioural changes in trace fossils to predict declining oxygen gradients. A stable oxygen gradient is often



Fig. 3.3. Ichnofaunal changes associated with a declining oxygen gradient showing the loss of the shallowest tiers and the shallower penetration of the deepest tiers. From Savrda and Bottjer (1987a).

#### A. GRADUAL DEOXYGENATION

#### **B. SUDDEN DEOXYGENATION**



**Fig. 3.4.** Predicted tiering patterns for (a) a gradual deoxygenation event (probably over a period of several thousand years) and (b) a sudden deoxygenation event of a few hundred to a few years' duration. The same tiering profile as Fig. 3.3 is assumed.

Chondrites Zoophycus Planolites Teichichnus Rhizocorallium			
Planolites Teichichnus Rhizocorallium			
Rhizocorallium		-	—i
Wignall (1991 <i>b</i> )			
Astacimorphichnu	3		1
Planolites	1		   
Rhizocorallium			
	Wignall (1991b) Astacimorphichnu Planolites Rhizocorallium	Wignall (1991b) Astacimorphichnus Planolites Rhizocorallium	Wignall (1991b) Astacimorphichnus Planolites Rhizocorallium Cho. chi

Fig. 3.5. Supposed oxygen-related ichnogeneric schemes. With the possible exception of *Chondrites*, all studies show little in common and highlight the difficulty of determining oxygen levels using this approach. A, aerobic; UD, upper dysaerobic; LD, lower dysaerobic.



Fig. 3.6. Bedding plane of *Astacimorphichnus* from the Freshwater Steps Stone Band, a coccolith limestone from the Kimmeridge Clay of Dorset.

associated with a decline in bottom-water energy and the abundance of suspended food. Thus suspensionfeeders' dwellings (domichnia) are predicted to decrease in number whilst horizontal migratory feeding trails (pascichnia) become more important in dysaerobic biofacies (e.g. Edwards, 1985). Pascichnial trace makers derive their oxygen from the interstitial sediments as they do not maintain contact with the sediment surface during feeding. As benthic oxygen levels decline the abundance of oxygen within the sediment becomes very limiting and fodinichnial traces, which maintain open contact with the sediment surface, become dominant in lower dysaerobic sediments. *Chondrites* is the obvious type example of this strategy. Ekdale and Mason's proposed domichnia-pascichnia-fodinichnia transitions can be produced by a change of grain size from coarse to fine. A pascihnia-fodinichnia transition may also be produced by an increase in the substrate cohesiveness of fine sediment without any implied change in the oxygen gradient. The model clearly fails to predict any aspect of the Kimmeridge Clay trace fossil assemblages (Fig. 3.5) and its predictive use is restricted to dysaerobic biofacies.

In summary, the most reliable use of trace fossils, as with all other palaeoecological indicators, lies in the diversity decline associated with an oxygen gradient. A decrease in burrow size may also occur, culminating in the tiny meiofaunal burrows of lowest dysaerobic/ poikiloaerobic biofacies, although these are infrequently seen as they only disrupt the finest lamination. *Chondrites* may be tentatively used as a lowest-oxygen indicator but more should be learnt of its substrate control and its temporal occurrence through the Phanerozoic.

#### 3.6 PALAEOECOLOGY OF A BLACK SHALE, THE KIMMERIDGE CLAY

In order to assess the utility of the RMB and shelf models, a detailed palaeoecological data set is presented from the Scitulus Zone, of the Kimmeridge Clay (Fig. 3.8). At its type locality on the coast of southern England the Kimmeridge Clay consists of decimetre to half metre-scale alternations of organic-rich shales and



Fig. 3.7. Interpretation of *Astacimorphichnus* bedding plane as a series of 'frozen' colonization events by cohorts of nematodes. At larger sizes the burrows begin to resemble *Planolites*. Reproduced from Wignall (1991b) with the permission of the SEPM.

mudstones with rare beds of coccolith limestone and dolostone (Fig. 2.7). Limestones are not seen in the Scitulus Zone although some mudstones are very marly. The dolostones are a diagenetic product of the replacement of the three other lithologies (Irwin *et al.*, 1977).

Geochemical and lithological data are also included here in order to independently assess palaeo-oxygen levels. Total organic carbon (TOC) and authigenic uranium values are generally higher the more prolonged the intervals of benthic anoxia during deposition (see Chapter 4 for fuller discussion). Absolute abundances of taxa are plotted, rather than the more usual percentage abundance, in order to give an impression of the 'fossiliferousness' of the sediments. Faunal diversity is given as the number of species present in each sample (species richness) but, as this is strongly sample-size dependent (Sanders, 1968), the Shannon index (H) has also been calculated:

$$H = -\sum_{i=1}^{i=S} p_i \ln p_i$$

where S is the species richness and  $p_i$  is the proportion of the ith species in the sample. High values of H not only indicate high species richness but also an even distribution. Unlike S, H is little affected by sample size, except at very small numbers (Wignall, 1990a).

During sampling note was also taken of the abundance of fish remains and their small phosphatic faecal pellets. Of all the fauna recorded from the Kimmeridge Clay fish show the least variation of abundance and diversity with lithology, presumably because they lived high in the water column and were little influenced by benthic conditions. The abundance of their faecal pellets can therefore be used as an approximate indicator of sedimentation rate. Similarly the ammonites of the Scitulus Zone (Pectinatites spp.) show little fluctuation in their abundance. This is not unexpected, because such nektonic organisms should be unaffected by benthic facies variations. However, they are to some extent facies-bound because ammonites are abundant in the basinal locations (such as Kimmeridge Bay) whilst in contemporary strata on the margins of the basin (best seen around Boulogne, northern France) they are absent even in fine-grained facies. This suggests that ammonites did not live around the basin margins and also that nekroplanktonic drifting must have been rare. The mode of life of ammonites, particularly their diet, is enigmatic but their discrete facies occurrences (e.g. Batt, 1989) suggest that they were nektobenthic rather than surface dwellers.

Bivalves dominate the fauna of the Scitulus Zone;

only in a thin shale of Bed 37e (Fig. 3.8) does the gastropod Semisolarium rival them in importance. The three shallow infaunal suspension feeding species Protocardia morinica, Nicaniella extensa, and Isocyprina minuscula are the commonest species and they can occur in prolific numbers (Fig. 3.9) whilst the remaining seven benthic species are very much rarer (Fig. 3.8). Mesomiltha concinna, a lucinid, probably pursued a chemosymbiotic life strategy whilst Semisolarium may have been a grazer but these are the only non-suspension feeders in the fauna. The three most common bivalves are also encountered in a wide range of other fine-grained facies (Oschmann, 1988a; Wignall, 1990a) indicating a wide environmental tolerance typical of opportunistic species. Their size varies from horizon to horizon, although on any one bedding plane only one, two or sometimes three distinct sizes are present, suggesting that distinct cohorts are preserved (Wignall, 1989). The bivalves are not unusually small in the organic-rich shales and, for Protocardia morinica, the largest specimens known of this species (up to 28 mm high) can be obtained from the shale of Bed 39c.

A rare, low-diversity fauna of foraminiferans also occurs within the Scitulus Zone. Agglutinating species *Amoebaculites* and *Proteonina* are found (Lloyd, 1959) along with the ubiquitous Jurassic opportunist *Lenticulina muensteri* (Wignall, 1990c). Microfossil preparation also revealed the common presence of ophiuroid ossicles. These are also seen in thin sections of the bivalve-bearing bedding planes (Fig. 3.10) and fully articulated specimens are known from higher in the Kimmeridge Clay (Ensom and Etches, 1987). It is difficult to quantify the disarticulated remains of ophiuroids and they represent a little appreciated aspect of the fauna.

Trace fossils are best seen in the Kimmeridge Clay coccolith limestones and at marked lithological junctions, particularly where mudstones overlie shales (Fig. 3.11; Wignall, 1991b). Here the mudstones have been piped down into the shales for a depth of 1 cm or less by simple meandering Planolites burrows, which occasionally show vaguely developed backfill. This lowdiversity pascichnial assemblage is presumably present but not seen throughout the thickness of the mudstones where it is responsible for destroying the fabric lamination of the type seen in the associated shales (e.g. Fig. 2.2). The Astacimorphichnus assemblages noted above from coccolith limestones represent transient colonization events that did not significantly disrupt lamination. The complete bioturbation of the mudstones indicates persistent benthic colonization, in contrast to the shales where the discrete shelly bedding planes indicate episodic colonization.

#### KEY



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Fig. 3.8. Graphic log and palaeoecological data set for the Scitulus Zone, Kimmeridge Bay, Dorset. The lithological log shows a weathering profile. Bed numbers (37a-40a) are from Wignall (1990a). Only sporadic TOC measurements are given below Bed 39a, whilst a more complete coverage is presented for authigenic U data, except for Beds 37f-38b. Faunal plots give absolute abundance based on sample sizes of approximately 0.02 m<sup>3</sup>.



Fig. 3.9. Bedding plane assemblage from an organic-rich shale of the Scitulus Zone consisting of large specimens of *Protocardia morinica* and smaller *Isocyprina minuscula*. Several specimens are still articulated but with their valves open.

The dominance of a suspension-feeding life strategy amongst the shelly taxa of the Scitulus Zone indicates that they belong to the poikiloaerobic biofacies of the shelf model. In comparison with the shales, with which they are interbedded, the mudstones are more organicpoor, contain less authigenic uranium, and have slightly higher species richness and H values, all suggesting more elevated benthic oxygen levels. The shelly fauna is essentially the same, although the mudstones must also have contained a fauna of soft-bodied deposit feeders. The conclusion that the mudstones represent slightly better benthic conditions than the shales has been noted in all previous studies of the Kimmeridge Clay (Morris 1980; Oschmann, 1988a; Wignall, 1990a; Wignall and Hallam, 1991). However, this is only true on the small scale. The Scitulus Zone sediments show an overall trend of a decline of oxygen levels upwards. Thus TOC and authigenic uranium values increase upsection whilst the absolute abundance, species richness, and H values of the fauna decline (Fig. 3.8). The increase in pelagic components such as faecal pellets indicates an associated decline in sedimentation rates. Thus, the mudstones of the upper Scitulus Zone (Beds 39a-40a) formed under lower oxygen levels than the shales of the lower Scitulus Zone. For example, the mudstone of Bed 39d contains 20 wt % TOC and three rare benthic species whilst the paper shale of Bed 38a contains only 12 wt % TOC and five common benthic species. Clearly the mudstone belongs to a lower dysaerobic/poikiloaerobic biofacies than the shale on the basis of all criteria except for its fabric.

Both the RMB and shelf model predict that laminated/fissile lithologies should occur under lower oxygen conditions than bioturbated mudstones. The example from the Kimmeridge Clay is therefore rather puzzling, but presumably benthic oxygen was persistently available during mudrock deposition, albeit in low concentrations, to allow a bioturbating fauna to destroy the preferred fabric orientation. The shales, on the other hand, record shorter oxygenated intervals, which may have been higher than those encountered in



Fig. 3.10. Thin section of an organicrich shale from the Elegans Zone of the Kimmeridge Clay showing an horizon of abundant bivalve shells and isolated ossicles of ophiuroids (arrowed).



Fig. 3.11. Junction between a pale, marly mudstone and an organic-rich shale in the upper Hudlestoni Zone of the Kimmeridge Clay. *Planolites* burrows penetrate down for around 1 cm into the underlying shale whilst the mudstones are completely burrow mottled. Note that this highly oblique wave-cut section gives an impression of a greater depth of burrowing at the contact.

the mudstones, interspersed with prolonged and truly anoxic conditions. The Scitulus Zone therefore consists of alternations of poikiloaerobic shales and dysaerobic mudstones. That the dysaerobic mudstones may record lower average benthic oxygen levels than some shales has not been previously recognized.

#### 3.7 OXYGEN-RESTRICTED BIOFACIES

From the foregoing section it is clear that the distinction between dysaerobic and poikiloaerobic biofacies is by no means clear, particularly if only short sections are available for analysis and the full facies range of the benthic taxa is not known. In order to overcome the problems of applying genetic classification schemes, an oxygen-restricted biofacies (ORB) scheme based solely on descriptive criteria, essentially benthic species richness, has been proposed (Wignall and Hallam, 1991). Species richness declines with oxygen level in both the RMB and shelf models and, as shown in Section 3.5, it also covaries with geochemical criteria used to assess oxygen levels. The ORBs can therefore be used to define palaeoenvironmental oxygen gradients, but unlike the genetic models they are not tied to precise dissolved oxygen concentrations.

A total of six ORBs have been defined, based on type examples from the British Jurassic succession although they are readily recognized throughout the Phanerozoic.

**ORB 1** is defined by the complete absence of any benthic or nektobenthic (ammonoid) species. Such biofacies contain only truly pelagic organisms such as fish and, in the Palaeozoic, graptolites, agnostids, and styliolinids (Berry *et al.*, 1989). Rare pseudoplankton may also occur, ideally still attached to their float (see Section 3.9). Fine-scale lamination is very common in ORB 1. Care must be taken to ascertain that the absence of a calcareous benthos is not due to dissolution. However, even if dissolution is intense, the fauna should be detectable as 'ghost' periostracal films. Concretions often preserve calcareous taxa from dissolution (Maples, 1986).

ORB 1 records permanently anoxic bottom waters and the absence of nektobenthos indicates that fully euxinic conditions may have occurred. Examples of ORB 1 are abundant in the graptolitic shales of the
Palaeozoic (e.g. Kemp, 1991) but they are much less common after the Silurian.

**ORB 2** faunas are again devoid of benthic taxa, although the nektobenthic ammonoids are present and may be abundant (Fig. 3.12). Oxygen was presumably present close to the sea floor to enable this fauna to survive, but the absence of benthos implies permanent anoxia at the sediment surface. ORB 2 is common in many Jurassic black shales (Wignall and Hallam, 1991); Ramsbottom's (1962) thick-shelled goniatite biofacies from the Carboniferous also belongs in this category.

ORB 3 faunas include between one and four benthic species in addition to the nektobenthic and pelagic forms of ORBs 1 and 2 (Fig. 3.13). Whilst ammonoids may again be common the benthos is exceedingly rare. Bivalves are the commonest benthic group and shallow infaunal or epifaunal types are common, but in the Posidonia Shale of Germany the deep infaunal Goniomya also occurs (Riegraf, 1977)-a most unusual occurrence in ORB 3. Ophiuroids are also frequently encountered in ORB 3 (Huckel, 1970; Dietl and Mundlos, 1972; Freels, 1975; Hemleben, 1977), particularly in lagoonal plattenkalks where oxygen-restricted deposition occupied a small area. From the Cretaceous onwards several benthic genera of foraminiferans appear to have been able to survive in lowest dysaerobic biofacies almost devoid of a macrobenthos-the quasi-anaerobic biofacies of Koutsoukos et al. (1990).

All examples of ORB 3 occur in fissile strata and lamination is common. Microburrows may be present but they do not penetrate to sufficient depth to disturb millimetre-thick laminae (Kemp, 1990; Wignall, 1991b). Identifying the meiobenthos responsible for the burrows is difficult, although scolecodont teeth have been recorded from laminated black shales (Courtinat and Howlett, 1990) as have small faecal pellets attributed to capitellids (Cuomo and Rhoads, 1987).

ORB 3 represents conditions in which very low benthic oxygen levels permitted only a few species to colonize for brief intervals of time. By comparison with the shelf model predictions, oxygenation events of only a few months are indicated. Perhaps only a few weeks of oxygenation are implied by the plattenkalk ophiuroids as the mobile adults could migrate into the basin before planktonic larvae settled and before anoxic conditions returned killing such 'hopeful pioneers'.

**ORB 4** faunas consist of between two and eight benthic species. Therefore there is commonly little increase in species richness over ORB 3. However, ORB 4 is characterized by a much greater abundance of benthic specimens (Fig. 3.13). ORB 4 sediments are commonly fissile and laminated with bedding planes covered in a few species of bivalve or brachiopod (Fig. 3.14) – the 'paper pectens' of Section 3.10. The shelly laminite facies of Hallam (1987) is directly equivalent to this biofacies whilst many of Savrda and Bottjer's (1987b) examples of exaerobic biofacies (Section 3.8.1) are equivalent to ORB 4.

Discrete shelly laminae interbedded with laminae devoid of benthos implies episodic colonization typical of the lower poikiloaerobic biofacies (Fig. 3.2). However, as noted in Section 3.6, species richness values of 2 to 8 can also occur in mudstones. In these examples the destruction of a preferred fabric orientation was



Fig. 3.12. Bedding plane covered in specimens of *Amoeboceras* from the Mutabilis Zone of the Kimmeridgian, Eathie. Cromarty, Scotland. An example of ORB 2; benthic forms are absent.



Fig. 3.13. Oxygen restricted biofacies defined by the number and abundance of benthic species. Based on Wignall and Hallam (1991) but with the recognition that some examples of ORB 4 can occur within non-fissile mudrocks.



Fig. 3.14. ORB 4 assemblage of *Dunbarella* and rarer *Posidonia* from black shales of the Gastrioceras listeri Marine Band, Westphalian, Upper Carboniferous of Bullhouse Quarry, Penistone, South Yorkshire.

probably achieved by prolonged bioturbation under persistently low benthic oxygen values. ORB 4 mudstones are therefore classified as a dysaerobic biofacies whilst the shales are a poikiloaerobic variety.

An alternative terminology for this dichotomy of

biofacies types was presented by Sageman (1989) in his detailed study of oxygen --restricted biofacies in the Cretaceous of the US Western Interior. He noted that lowest oxygen environments could be recorded either by laminated, shaly facies replete with inoceramid bivalves or by mudstones with an impoverished trace fossil assemblage. The former he termed a benthic boundary biofacies and the latter an 'unbounded' biofacies. Sageman ascribed the difference between these two biofacies to the presence of a bacterial mat in the former which inhibited burrowers. No distinction in the oxygen regimes was implied. This interpretation is not valid for the Kimmeridge Clay example (Section 3.6) as infaunal species are abundant in both the 'bounded' and 'unbounded' biofacies. As outlined above. I consider the fabric differences in the variants of ORB 4 to be due to variations in the duration of oxygenation events.

**ORB 5** faunas consist of between five and ten species although, unlike the preceding ORBs, the richness is strongly controlled by sample size. Thus Duff's (1975) bituminous shale biofacies from the Jurassic Oxford Clay contains nearly 30 benthic species although only nine are common. Therefore ORB 5 is best defined by the presence of up to ten *common* species. Many of the late Palaeozoic dysaerobic faunas recorded by Kammer *et al.* (1986) belong to ORB 5. A moderate diversity of groups is present, including archaeogastropods and nuculoids as well as the suspension feeding bivalves seen in ORBs 3 and 4. A weak fissility may be developed in some examples (e.g. Duff, 1975) but in general massive mudstones occur and fine lamination is never seen.

ORB 5 sediments record more persistent/elevated benthic oxygen levels although the relatively low diversity still indicates oxygen restriction. ORB 5 sediments can contain a respectable amount of organic carbon; up to 10 wt % TOC is known from the Oxford Clay (Hudson and Martill, 1991).

**ORB 6** faunas consist of at least ten common benthic species and Kammer *et al.* (1986) consider that up to 40 benthic species can occur in dysaerobic strata. The higher values would be worthy of many aerobic biofacies and additional criteria are necessary to detect the influence of dysoxic bottom waters. ORB 6 is thus also defined by the absence of stenoxic taxa. These include many groups of crinoids, all corals, and thick-shelled taxa. The deep infaunal tier occupied by many bivalves in the post-Palaeozoic is not developed under even slightly oxygen-restricted conditions with the exception of the chemosymbiotic lucinaceans found in Jurassic ORB 6 examples (Wignall, 1990a; Wignall and Hallam, 1991).

The oxygen-restricted biofacies scheme has been utilized to detect temporal trends in a Kimmeridgian succession (Wignall and Pickering, 1993) and it also has the potential to depict palaeogeographical variations in much the same way as the organic facies concept has been used to summarize basin-scale organic geochemical data bases (e.g. Baudin *et al.*, 1989).

# 3.8 FURTHER TERMINOLOGY

#### 3.8.1 Exaerobic biofacies

The exacrobic zone and biofacies concept was introduced by Savrda and Bottjer (1987b) for the horizons of *Anadara montereyensis* (a shallow infaunal suspensionfeeding bivalve) recorded at the junctions between laminated and burrowed strata in a short section of the Miocene Monterey Formation of California. As abundant bivalves are not predicted to occur in dysacrobic biofacies of the RMB model, Savrda and Bottjer proposed their new biofacies and positioned it at the anaerobic/dysacrobic divide (Fig. 3.1(c)). They suggested that the fauna consisted of chemosymbionts even though no modern *Anadara* species or its relatives pursue this life strategy. As originally defined, the exacrobic biofacies are essentially identical to Hallam's (1987) shelly laminite facies with the addition of chemosymbiotic connotations, but there have subsequently been substantial modifications.

Savrda et al. (1991) and Savrda and Bottjer (1991) redefined the exacrobic biofacies as occurrences of in situ chemosymbiotic, epibenthic bivalves and brachiopods in laminated strata. Ironically this excludes the original type example from the biofaces for A. montereyana occurs on, not within, laminated strata and it is an infaunal not epifaunal species! They also proposed that exacrobic 'environments were normally anoxic but periodically experienced episodes of reoxygenation' (Savrda and Bottjer, 1991, p. 211), an interpretation reached in many previous studies of black shale faunas from epicontinental seas (e.g. Wignall and Myers, 1988; Oschmann, 1988a; Sageman, 1989). However, it is not valid to include the concept of environmental instability within one of the biofacies of the RMB model for this is based on a stable environmental continuum. It is for this reason that Oschmann (1991) has introduced a separate poikiloaerobic concept which I follow with slight modification here. Savrda, and Bottjer further consider that infaunal taxa (excluding their type example presumably) were inhibited in their exaerobic biofacies by the presence of bacterial mats and they list the presence of a specialized grazing fauna of ostracods, foraminifera and small echinoids as evidence for their former presence.

The exacrobic biofacies now has very precise environmental connotations—chemosymbionts thriving on bacterial mats during brief oxygenation events. But, as discussed in Section 3.3, chemosymbiosis is a highly unlikely strategy in dysoxic environments whilst the common presence of infaunal species in black shales indicates that bacterial mats do not always occur in lower dysaerobic biofacies. In fact, in all modern settings, bacterial mats are rapidly consumed once oxygen levels are sufficient to sustain a grazing fauna, and it is perhaps unlikely that bivalves could grow on such substrates before they were eaten.

# 3.8.2 Morris' scheme

Morris (1980) utilized data from British Jurassic black shale faunas to propose an oxygen-restricted shale classification scheme. By plotting the relative proportions of bivalve life strategies on a ternary diagram he showed that **normal shales** should be dominated by infaunal suspension feeders, **restricted shales** by deposit feeders, and **bituminous shales** by epifaunal suspension feeders. The restricted and bituminous shales roughly correspond to upper and lower dysaerobic/poikiloaerobic biofacies respectively. This scheme is, however, invalidated by major errors in Morris' data set (Morris, 1980, Tables 3 and 4). His Kimmeridge Clay fauna supposedly consists of epifaunal suspension feeders and deposit feeders but in fact infaunal suspension feeders are wholly dominant at the levels he studied. Also his Oxford Clay data set is taken from Duff (1975) in which the abundant epifaunal suspension feeding fauna of *Bositra* and *Meleagrinella* have been removed from some of the analyses thus giving an apparently deposit-feeder-dominated assemblage. Morris also appears to have included gastropods in his Oxford Clay data set and plotted them on the bivalve ternary plot.

As shown in the discussion of shelf faunas (Section 3.2), bivalve trophic groups have little relationship to oxygen tolerance.

#### 3.9 PSEUDOPLANKTON

Many older studies assumed that all benthic-like taxa encountered in black shales were pseudoplanktonic/ pseudopelagic forms that had become detached from floating objects in the water column and descended to the seafloor. The justification for this interpretation stemmed from the supposedly anoxic and therefore hostile benthic conditions necessary for black shale formation. Over the past two decades the development of the concept of dysaerobic biofacies and the realization that organic-rich shales could form in oxygen-poor but not anoxic bottom waters, has caused many recent studies to interpret benthic taxa as truly in situ. However, many authors still assume that all black shale faunas are pseudoplanktonic (e.g. Thayer, 1974; Watkins, 1978; Barron and Ettensohn, 1981; Schumann, 1988; Leeder et al., 1990). Commonly there is little justification for these interpretations, and in many cases they are functionally impossible (e.g. the epipelagic lifestyle proposed for infaunal lingulids by Thayer (1974) and Barron and Ettensohn (1981)). A detailed study of the criteria neccessary for assessing pseudoplankton is given in Wignall and Simms (1990) and only a brief summary is given here.

Ideally pseudoplanktonic forms should be found still attached to their float (Fig. 3.15). A diverse range of floating substrates is available including driftwood, pumice, vesicular algae such as the present day *Sargussum*, and cephalopods, particularly the externally shelled ammonoids which were common in the world's oceans until the end-Cretaceous. With the exception of algae, all of these substrates can also be colonized after they have sunk to the sea floor making it difficult to interpret the timing of epizoan colonization. For ammonoids a series of criteria can be used to dis-



Fig. 3.15. Ammonite colony consisting of a *Cunegervillia* attached to a *Plagiostomu* which is in turn attached to a juvenile ammonite. The pseudoplanktonic interpretation is supported by the occurrence of the bivalves on the lower ventral edge of the ammonite and the absence of any associated benthos at this horizon. From the Shales-with-Beef Formation, Sinemurian, Lower Jurassic of Charmouth, Dorset.

tinguish benthic from nektonic infestation (Seilacher, 1960, 1982a; Wignall and Simms, 1990):

(1) If infestation occurred in the water column, both flanks of the ammonoid should contain epizoans.

(2) As the infestation is essentially a matter of chance encounters between the planktonic larvae of epizoans and the ammonoid, older and therefore larger shells are more likely to be colonized. By the same line of reasoning, the umbilical region is most likely to be encrusted rather than the last-formed body whorl. The opposite pattern holds for benthic colonization as the body whorl is likely to be more elevated above the substrate.

(3) Epibionts represent unwanted ballast on the host ammonoid and they are therefore likely to have developed mechanisms to defend themselves. The success of these strategies is likely to have varied from species to species and there will therefore be a taxon-specific variation in the degree of epizoan overgrowth (Seilacher. 1982a). More streamlined ammonites in particular should have fewer epibionts. For example, Doyle and Whitham (1991) have noted that *Torquatisphinctes* from black shales of the Nordenskjold Formation have abundant oxytomids covering their umbilical regions whilst *Virgatosphinctes* has no associated epibionts. Such taxon-specific colonization would not occur once the ammonites had died and sunk to the sea floor.

# 34 Palaeoecology

The above criteria have been applied to a large sample size of ammonites (many encrusted by *Liostrea*) from Kimmeridgian black shales of Scotland (Wignall and Pickering, 1993). The results showed that generally only the larger ammonites were encrusted in their umbilical region, implying pseudoplanktonic colonization. However, very few ammonites were seen to be encrusted on both flanks, indicating that the first criterion given above may not always be reliable. Also, it is often difficult to examine and distinguish both flanks of ammonoids when they have been crushed during compaction. The third criterion could not be applied as the sample consisted almost exclusively of one species.

Many pseudplanktonic species utilize a pendent life strategy where the attachment area is relatively small compared with the overrall size of the organism (Wignall and Simms, 1990). The modern day goose barnacles are a classic example of this as are the Jurassic crinoids *Seirocrinus* (Simms, 1986). This minimizes the area occupied on the float, which is often at a premium, but it increases the chance of dislodgement. Many, if not most, pseudoplanktonic specimens are no longer associated with their float. The following criteria can be used to determine their mode of life:

(1) Pseudoplankton should have the means to attach to a float. Byssal attachment, pedicle attachment, boring, clinging (e.g. gastropods), and cementation are the main strategies.

(2) Pseudoplanktonic species should have a very widespread facies distribution as they are not influenced by the benthic environment.

(3) Pseudoplanktonic specimens should always be very rare as the potential attachment sites in the pelagic realm are very few compared to the vast abundance of available habitat area for epizoans in the benthic realm. Under the exceptionally slow sedimentation rates encountered in some black shale environments pseudoplankton may become common but other truly pelagic forms such as fish, graptolites, and ammonoids should also be common at such horizons.

### 3.10 PAPER PECTENS

Central to the debate on the validity of benthic/ pseudopelagic black shale faunas and exaerobic versus poikiloaerobic interpretations are the epifaunal, thinshelled, flat-valved bivalves (and brachiopods in the Palaeozoic), which are commonly prolific in examples of ORB 4. I have loosely termed this group the 'paper pectens' (Wignall, 1990b) based upon their morphological rather than their taxonomic features. As there are no similar taxa known from modern dysoxic settings (except perhaps for the tantalizingly brief note of Soutar *et al.* (1981)), their mode of life has been the subject of substantial debate.

Prior to the Carboniferous, Cardiola and Buchiola are the most commonly recorded black shale bivalves (Berry and Boucot, 1967; Watkins, 1978). Their equivalved, moderately inflated form, with a truncated posterior margin, is indicative of a shallow infaunal lifestyle, despite claims for their pseudoplanktonic origin (Watkins, 1978; Kammer et al., 1986). The first true paper pectens appeared in the Devonian (Pterinopecten and Pterochaenia) and they are the dominant morphotype in ORBs 3 and 4 from the Carboniferous to the Cretaceous. Paper pectens are also found in ORBs 5 and 6, where they commonly occur in swarm abundances that are unrelated to fluctuations of the benthic taxa (e.g. Wignall and Pickering, 1993). This divorce of paper pecten ecology from normal benthic ecology led Duff (1975) to separately assess the paper pectens and the benthic taxa in his palaeoecological analysis of the Oxford Clay.

The majority of paper pectens belong to the Aviculopectinacea, Pectinacea, and Pteriacea Superfamilies although several genera also occur in unrelated groups. *Pterochaenia* is a lunulacardiid for example, whilst the Buchiacea produced *Anningella* and *Claraia*. Many of the paper pectens are only found in black shales, although *Bositra buchi* in the Jurassic and many species of *Daonella* and *Halobia* are also abundant in micritic limestones where they may occur in rock-forming abundances such as the filamentous limestones of Tethys (Conti and Monari, 1992). The common red coloration of such limestones indicates oxic depositional conditions and the only common factor with black shale environments is the very fine-grained substrata.

The paper pecten category includes three distinct and relatively discrete morphologies that repeatedly evolved in many separate lineages (Fig. 3.16). The mytiliform bivalves are still common today, whilst dunbarelliform and posidoniform bivalves represent some of the few entirely extinct bivalve morphologies. That the paper pecten classification scheme is not an entirely artificial construct is indicated by the very different evolutionary rates exhibited by bivalves of these groups. Presumably this indicates different lifestyles and eco-evolutionary pressures. Species duration of posidoniform and mytiliform paper pectens is typically in excess of several million years—a value common for many bivalves. For example, *Bositra buchi* lasted from the Toarcian to the Oxfordian of the

PAPER PECTEN N	MORPHOTYPES
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	DESCRIPTION	EXAMPLES		
Dunbarelliform	Hinge line around maximum width with centrally placed umbone. Fine radial ribs are the dominant ornament. Circular outline. Some varieties, such as <i>Dunbarella</i> , are inequivalved with an auriculate right valve but others such as <i>Daonella</i> are equivalved.	Dunbarella, Pterinopecten, Claraia, Daonella, Halobia, Aulacomyella.		
Posidoniform	Hinge line shorter than maximum width, umbone centrally placed. Concentric ornament. Circular to elongate outline. Equivalved and usually with anterior and posterior gapes.	Posidonia, Bositra, Steinmannia, Inoceramya.		
Mytiliform	Medium length hinge with umbone at anterior end. Weak ornament. Trigonal to quadrate outline.	Posidoniella, Selenimyalina, Caneyella, Plagiostoma, Parainoceramus, Pterochuenia, Pseudomytiloides, Anningella, Semuridia.		

Fig. 3.16. Proposed classification of paper pecten morphotypes.

Jurassic, a period of 35 million years. In contrast the dunbarelliform paper pectens exhibit amongst the fastest and most unusual evolution of any bivalve group. In the Namurian (Upper Carboniferous) of Europe species of Dunbarella succeed one another every one to two million years. In the Triassic, nearly a dozen species of Daonella appear around the Anisian/Ladinian boundary (Rieber, 1969, Fig. 5); Claraia exhibits a similar pattern in the early Triassic (Yin, 1985). The high turnover and widespread occurrence of such forms makes them ideal biostratigraphic markers (e.g. Kelly and Doyle's (1991) Aulacomyella-based scheme). It could be argued that such high evolutionary rates are an inevitable consequence of the exquisite detail available for study in dunbarelliform bivalves. This is readily discounted, however, by the numerous examples of equally well-ornamented, but slowly evolving bivalves. For example, Aviculopecten aff. losseni is found throughout the Namurian whilst eight species of Dunbarella come and go over the same interval.

The number of proposed modes of life of paper pectens is probably greater than for any other extinct group (Fig. 3.17), but, as discussed below, the palaeoecological justification for many of these alternatives is rather dubious. (1) Pseudoplankton. Undoubtedly the most popular invoked lifestyle is that of attachment to drifting/ floating objects (Bonardi, 1970; Rieber, 1982; Schumann, 1988). As dunbarelliform and posidoniform paper pectens are commonly too abundant to have been derived from driftwood colonies, Sargussum-like seaweed colonies are usually inferred. However, the highdiversity epizoan assemblages on modern Sargussum makes them poor analogues for the typically mono- or paucispecific paper pecten assemblages.

A pseudoplanktonic lifestyle may be valid for many mytiliform paper pectens as they are commonly less abundant and examples of colonies attached to driftwood and seaweed are known (Seilacher, 1982b; McRoberts and Stanley, 1989). It is significant that no dunbarelliform or posidoniform bivalves have ever been found associated with such floats.

(2) Nektonic. Jefferies and Minton (1965) challenged the pseudoplanktonic interpretation for posidoniform bivalves (particularly *B. buchi*) on the grounds that they lacked a byssus and therefore a means of attachment. But, they noted that their widespread geographical occurrence suggested a pelagic life-style and they therefore proposed an active swimming existence.

A life of persistent, energetic flapping seems rather



Fig. 3.17. Diagram illustrating the many proposed modes of life for paper pectens. A. Epiplanktonic. B, Nektonic. C, Teleplanic larvae. D, Epibenthic attached to benthic algae. E, Pelagobenthic attached to floating benthic algae. F, Epibenthic. G. Epibenthic mudstickers. H, Epibenthic chemosymbionts.

unlikely for bivalves. In fact, *B. buchi* has byssal retractor muscle scars (Kauffman, 1981) and is an epibyssate form like all other paper pectens. The restriction of this bivalve to fine-grained facies rather than a wide range of facies types also argues against a nektonic existence.

(3) Planktonic larvae. In a similar vane to Jefferies and Minton, Oschmann (1993) suggests that *B. buchi* and other similar paper pectens may be a form of giant plankton. The teleplanic larvae of some leptonacean bivalves are held as modern analogues even though these reach only a few millimetres in height and their shells are proteinaceous and uncalcified (Allen and Scheltema, 1972). This contrasts with the much larger size of many paper pectens, some of which can reach 8 cm in height. In many paper pectens there is a clearly marked transition from the planktonic larval shell to the juvenile and adult benthic shell (Fig. 3.18).

(4) Epibyssate. Many studies have assumed that, like other epibyssate bivalves, paper pectens were benthic (e.g. Weigelt, 1922; Craig, 1954; Wignall, 1987; Doyle and Whitham, 1991; Conti and Monari, 1992) although the attachment site remains a subject for speculation. Campbell (1985) suggested benthic algae for Daonella and Halobia and thereby implied that black shales accumulate within the photic zone. But, as with Sar-



**Fig. 3.18.** Specimen of *Dunbarella papyracea* from the same locality as Fig. 3.14 showing the morphological change from the inflated larval shell to the flat-valved benthic stage.

gussum, benthic algae are associated with a diverse range of epibionts, particularly within their holdfasts, none of which are seen in paper pecten assemblages. To partly circumvent this problem Duff (1975) suggested floating benthic algae as attachment sites (Fig. 3.17E).

In fact the paper pectens are most likely to have lain on the bottom where their broad flat valves may have prevented them from sinking into soft substrates. If paper pectens are snow-shoe strategists then this explains their restriction to fine-grained facies. They may have used their byssal threads to anchor to one another; a mutually supporting mat of interlinked bivalves is less likely to founder than unlinked individuals (Hollingworth and Wignall, 1992). Doyle and Whitham (1991) have described bedding planes covered in *Aulacomyella* with nests of *Buchia* on their upper surface (Fig. 3.19). The *Aulacomyella* may have converted a soft substrate into a shelly one available for

Antia and Wood (1977) suggested that *Bositra* may have been a mud-sticker (Fig. 3.17G) based on a few specimens preserved in this (life?) position although the morphology of *Bositra* is totally unlike the wedgeshaped morphology of known mudstickers such as *Pinna*. However, several species of *Daonella* approach this shape and they may indeed have lived in this position.

other bivalves.

Paper pectens are the defining fauna of the new version of the exaerobic biofacies, discused above, and they are therefore interpreted as chemosymbionts. Seilacher (1990) has further suggested that the byssal tube of *Halobia* may in fact be a pump for hydrogen



Fig. 3.19. Bedding plane covered in difficult to discern *Aulacomyella* colonized by a nest of *Buchia* from the Upper Jurassic Nordenskjold Formation of Antarctica. The presence of a covering of *Aulacomyella* may have enabled the *Buchia* to colonize a substrate which was otherwise too soft. From Doyle and Whitham (1991) with the permission of the authors and the Geological Society.

sulphide, although why this is focused at the umbone rather than on the gills is not explained. As already outlined, this life strategy is unlikely in black shales; paper pectens were presumably suspension feeders.

# 3.11 THE GREAT POSIDONIA SHALE DEBATE

The concluding section of this palaeoecological chapter illustrates the difficulty of black shale interpretation with the famous debate on the depositional conditions of the Lower Jurassic Posidonia Shale. This exemplifies the need to make detailed observations of black shale palaeoecology, although, even when faced with the same data, more than one interpretation is possible.

The Posidonia Shales are part of a widespread interval of organic-rich deposition in the Early Toarcian of Europe and elsewhere (Jenkyns, 1988). In its typical development in southern Germany, it consists of between 3 and 13 m of highly organic-rich shale with minor limestones and carbonate nodules. At the base and top of the unit, prolific numbers of Bositra cover bedding planes-a typical development of ORB 4. The central part of the unit contains abundant ammonites and Pseudomytiloides dubius (Kauffman, 1978). Small, thin-shelled gastropods are common in many of the concretions but they are absent from the shales, probably due to dissolution. The central part of the Posidonia Shale also yields exceptionally preserved marine vertebrate skeletons and giant driftwood colonies of P. dubius and Seirocrinus.

The Posidonia Shales are 'traditionally' considered to have accumulated beneath the stagnant, anoxic bottom waters of a silled basin somewhat analogous to the present day Black Sea (e.g. Seilacher and Westphal, 1971). *P. dubius* and other epibenthic bivalves are said to have fallen off floating substrates such as driftwood (Fig. 3.20). The discovery that many horizons contain evidence for strong bottom current activity (belemnite preferred orientations) lead Brenner and Seilacher (1978) to suggest that infrequent high-energy events punctuated the long term stagnant conditions.

Kauffman (1978, 1981) has strongly challenged this traditional view. He noted that *P. dubius* specimens were probably epibenthic as they are many orders of magnitude too abundant to have been derived from the relatively rare driftwood in the Posidonia Shale. He also noted the presence of the rare, but unequivocally benthic, bivalves *Goniomya, Solemya*, and *Unicardium*. A more diverse assemblage, including pseudomonotids and serpulids, occurs on the whorls of many of the larger ammonites. As this fauna is apparently



**Fig. 3.20.** Diagrams illustrating the proposed environmental conditions of the Posidonia Shale of southern Germany. Left: the 'traditional' model (e.g. Seilacher and Westphal, 1971) in which all benthic taxa are said to be pseudoplanktonic. Right: Kauffman's (1978, 1981) model with a sharp oxygen gradient across the sediment surface and a considerable diversity of benthos, particularly attached to ammonite benthic islands.

restricted to the upper flanks of ammonites lying horizontally within the sediment, Kauffman interpreted the ammonite shells as benthic islands which raised the epizoan communities above harmful anoxic conditions at the sediment surface. Thus Kauffman proposed that Posidonia Shale deposition occurred beneath a fully oxygenated water column in which anoxic substrates prevented the establishment of any infaunal benthos (Fig. 3.20). Modern organic-rich substrates are anoxic to within a millimetre of the sediment surface, but they are readily colonized by diverse endobenthic forms which can irrigate their burrows if the overlying bottom waters are oxygenated (Andersen and Halder, 1987). Kauffman therefore proposed the presence of an algal (cyanobacterial?) mat that maintained a sharp redox boundary at or near the sediment surface and prevented burrowing.

Kauffman's contentious model inevitably provoked a response. Seilacher (1982b) suggested that much of the driftwood in the Posidonia Shale seas was cast ashore and not preserved, thus causing the discrepancy between the abundance of *P. dubius* and driftwood. However, as Kauffman had noted, this fails to account for the abundance of *P. dubius* on some bedding planes

and its rarity or absence on others—an unlikely distribution for pseudoplanktonic forms. However, the functional morphology and taphonomy of the large, driftwood-attached *Seirocrinus* colonies appears to indicate a pseudoplanktonic origin (Simms, 1986).

Kauffman's ammonite benthic island hypothesis has also been questioned. Seilacher (1982a) showed that epizoan colonization was species-specific and occurred on both flanks of the ammonite. In fact, the poorly preserved condition of Posidonia Shale ammonites (highly flattened and decalcified) makes it difficult to discern on which side epizoans occur. The persistent presence of an algal mat hypothesis is also open to doubt. Bandel and Knitter (1986) noted that fish and vertebrate carcasses commonly sank several tens of centimetres into the substrate, suggesting a very soft consistency. Nonetheless, several other authors consider that bacterial/fungal mats were present during Posidonia Shale deposition (Riegal *et al.*, 1986; Loh *et al.*, 1986).

It is probable that bottom-water anoxia was typical of much of Posidonia Shale deposition, but, as Kauffman showed, even this most 'anoxic' of black shales contains evidence for benthic colonization events.

# Inorganic geochemistry

The previous chapter outlinesthe numerous techniques and approaches available for determining palaeooxygen values from palaeoecological information. Such conclusions are at their most definitive when corroborated by independent criteria; thus it is the aim of this chapter to review the wide range of inorganic geochemical indices available for assessing past oxygen levels. However, in order to discuss the various approaches it is first necessary to compare the diagenesis of fine-grained sediments beneath oxygenated and anoxic bottom waters.

# 4.1 DIAGENESIS BENEATH OXIC BOTTOM WATERS

The fundamental process controlling the various zones of diagenesis is the bacterial oxidation of organic matter. The zones reflect the sequential use of oxidants which are progressively less efficient and which therefore yield less free energy (Fig. 4.1) until, in the final methanogenic zone, carbon dioxide is produced by the direct bacterial breakdown of organic matter in the absence of an oxidant (Berner, 1980). The resultant



DIAGENESIS BENEATH OXIC BOTTOM WATERS

Fig. 4.1. Characteristics of diagenetic zones beneath oxic bottom waters defined by organic matter oxidation pathways. Based on references in text, particularly Canfield and Raiswell (1991a, b). Free energy values from Berner (1980).

diagenetic zones are discrete, thus sulphate reduction only occurs after all the oxygen has been consumed. The cause of the discrete boundaries is not clear, but it could be due either to intense competition between the bacteria or, the poisoning of the bacteria of one zone in the chemical conditions of the other (Laanbroek and Veldkamp, 1982; Jørgensen, 1982). For example, sulphate-reducing bacteria outcompete methanogenic bacteria for organic substrates as they utilize a more energetic pathway (Oremland and Taylor, 1978; Jørgensen, 1983): alternatively the presence of sulphide in the sulphate reduction zone (SRZ) may poison methanogenic bacteria.

#### 4.1.1 The oxic zone

The depth of the oxygenated surface layer is controlled by the rate of oxygen consumption, which is dependent primarily on the abundance of organic matter and the sedimentation rate. A 10 cm thick oxic zone is typical (Jørgensen, 1977; Revsbach et al., 1980) but, in highly organic-rich sediments, the irrigated burrows of infaunal organisms may constitute the only part of this zone (Jørgensen and Revsbach, 1985). In the oxic zone the production of CO<sub>3</sub> during organic matter breakdown tends not to lower the porewater pH as most CO<sub>2</sub> escapes from irrigated sediments. Bioturbation can also affect the pH in the underlying sulphate reduction zone by allowing oxidation of sulphides and ventilating any alkalinity increase in the porewaters. Both these processes favour carbonate undersaturation and may even lead to carbonate dissolution at this level (Fig. 4.1; Canfield and Raiswell, 1991b). The low values of pH achieved at this level may favour phosphate precipitation (Benmore et al., 1983) if there is sufficient phosphate available from organic matter. However, much of the available phosphorus is recycled into the bacterial biomass (Jørgensen, 1983).

#### 4.1.2 The denitrification zone

Once all the available oxygen in the porewaters has been used, a narrow zone of denitrification occurs in which bacterially mediated organic matter degradation continues but with nitrate as the oxidant. Only a few per cent of the organic matter is destroyed by this oxidation process (Canfield and Raiswell, 1991b), possibly up to a maximum of 20% (Jørgensen, 1983). Like the oxic zone, the porewaters remain slightly acidic further dissolving carbonate shells.

#### 4.1.3 The sulphate reduction zone

Once nitrate has been utilized, dissolved sulphate is the next major oxidant available and the bacterially controlled reaction with organic matter is:

$$(CH_2O)_x(NH_3)_y(H_3PO_4)_z + 0.5SO_{42-} - xHCO^{3-} + 0.5H_2S + yNH_3 + zH_3PO_4.$$

The combined effect of these products can initially cause an increase in acidity as, with the exception of NH<sub>3</sub>, all the decay products are weak acids (Ben Yaakov, 1973). Under these circumstances, the porewaters generally retain the carbonate undersaturation which results from a previous phase of aerobic activity. As the H<sub>2</sub>S is removed from solution to form iron sulphides, the porewaters become progressively more alkaline and carbonate saturation will occur. However, if deep burrows actively and regularly penetrate the SRZ (as would be expected in a fully oxygenated environment) alkalinity build up is prevented and dissolution can occur (Aller, 1982).

Much hydrogen sulphide is oxidized at the redox boundary but a significant proportion is fixed by reaction with iron. Initially, mackinawite (FeS) is formed (via a bacterially mediated pathway) which reacts with elemental sulphur to form framboids of greigite (Fe<sub>3</sub>S<sub>4</sub>). Ultimately pyrite (FeS<sub>3</sub>) forms, commonly by pseudomorphing the greigite framboids (Fisher and Hudson, 1987; Canfield and Raiswell, 1991a). The source of elemental sulphur used in pyrite formation and the nature of the oxidising reaction necessary to produce it are not well understood (Berner, 1970; Boudreau and Canfield, 1988; Canfield and Raiswell, 1991a), although intermediary sulphur oxidation states, such as thiosulphate  $(S_2O_3^{2-1})$ , may be important (Jørgensen and Bak, 1991). The intermediary stages of pyrite formation are highly unstable and the transition of FeS to FeS, may take place in as little as ten years (Jørgensen, 1977). Under conditions of low sedimentation rates and/or low sulphate reduction rates pyrite may form by direct reaction of Fe<sup>2+</sup> with H<sub>3</sub>S (Raiswell, 1982), as observed today in the Gotland Basin of the Baltic (Boesen and Postma, 1988).

The peak of carbonate saturation, and hence porewater alkalinity, is reached towards the base of the SRZ where isotopically light methane, diffusing up from the underlying methanogenic zone, is oxidized to CO<sub>2</sub>. Under conditions of very slow sedimentation or pauses in sedimentation carbonate concretions may grow at this site (Canfield and Raiswell, 1991b). These are characterized by light values of  $\delta^{13}$ C around -25%(Irwin *et al.*, 1977) inherited from the methane.

#### 4.1.4 The methanogenic zone

The methanogenic zone is only well developed if significant amounts of organic matter have survived their passage through the overlying zone. This may be favoured if there is originally a high flux of organic carbon to the sediment and/or sedimentation rates are high. During organic matter breakdown, the light carbon isotope is fractionated into methane whilst the carbon dioxide is heavy. Any carbonate concretions formed in this zone are consequently heavy, with  $\delta^{13}$ C values around +15% (Irwin *et al.*, 1977).

### 4.2 DIAGENESIS BENEATH ANOXIC BOTTOM WATERS

Beneath anoxic bottom waters diagenesis is somewhat simpler due to the absence of the oxic zone and the lack of burrows which impart the considerable geochemical heterogeneity seen in aerobic sediments. Most organic matter is degraded within the SRZ and large amounts of hydrogen sulphide are evolved. The lack of burrowing allows alkalinity build-up in the porewaters and thus carbonate fossils are commonly well preserved in black shales (e.g. Hudson and Martill, 1991). The converse is also true, with poor preservation being well known (Fig. 4.2); this is because, in many anoxic settings, pyrite formation is limited by the amount of iron available for reaction. This causes the build-up of hydrogen sulphide, a weak acid, in the lower part of the SRZ and



Fig. 4.2. Specimens of *Pseudomytiloides dubius* from the Posidonia Shale of southern Germany. The original calcitic shell has dissolved during early diagenesis leaving the characteristically wrinkled periostracal foil.

leads to carbonate dissolution (Canfield and Raiswell, 1991b).

The extent of organic matter oxidation in sediments accumulating beneath anoxic bottom waters may be considerably less than in oxic environments (see discussion in Chapter 6). This may be due in part to sulphate-reducing bacteria relying on a supply of simple organic acids, principally derived from heterotrophic bacteria in the oxic zone (Boreham and Powell, 1987). Additionally, bacterial lipids may preferentially survive under anoxic conditions (Emerson and Hedges, 1988). Sulphate reducing bacteria are also thought to be inhibited by the presence of their by-product, hydrogen sulphide (Boreham and Powell, 1987). This is generally removed from solution by precipitation as iron sulphide, but in many intensely anoxic environments sulphide formation becomes limited by the availability of reactive iron (Raiswell and Berner, 1985). The contention that black shales with iron-limited pyrite formation show evidence for better organic matter preservation has yet to be tested, although organic-rich carbonates (which contain very little reactive iron and therefore little pyrite) are known to be amongst the best hydrocarbon source rocks (Palacas et al., 1984).

With the exception of the oxic zone, all sediments pass through the same stages of diagenesis beneath oxygenated and anoxic waters. However, the resultant sediment chemistry is still highly distinctive. Beneath fully oxygenated bottom waters most sedimentary iron sulphides are re-oxidized at the redox boundary and never incorporated into the geological record. Similarly, in dysoxic conditions, pyrite is constantly oxidized and re-precipitated; only in voids such as the internal chambers of ammonites does pyrite avoid oxidation (Hudson. 1982). Large amounts of H<sub>2</sub>S are produced, and much larger amounts of pyrite are found in the sediment. In anoxic conditions virtually all pyrite is preserved, including prolific numbers of microscopic framboids.

### 4.2.1 Pyrite sulphur isotopes

Pyrite sulphur isotopes can be used in the evaluation of black shale depositional conditions. Bacteria tend to select the light sulphur isotope during sulphate reduction—a process which is more efficient under slower sulphate reduction rates (Kaplan and Rittenberg, 1964; Goldhaber and Kaplan, 1975). Thus Maynard (1980) demonstrated the close relationship of very light  $\delta^{34}$ S values and condensed black shale sections. Light sulphur isotopes are also produced by the repeated oxidation and recrystallization of-iron sulphides that occurs around the redox boundary (Fisher, 1986). The

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lack of bioturbation in anoxic and suboxic settings encourages the development of a closed system in the SRZ with the result that sulphur isotopes become progressively heavier during pyrite formation (Love *et al.*, 1983; Fisher and Hudson, 1987).

In summary, inorganic geochemical phenomena can provide valuable clues to former environmental conditions (Fig. 4.3). However, there has thus far been little attempt to distinguish between conditions of stable lowoxygen environments (dysaerobic facies) and fluctuating low-oxygen/anoxic environments (poikiloaerobic facies). The presence or absence of burrowers is probably one of the fundamental controls on facies type, and unburrowed lower poikiloaerobic facies will presumably have a more anoxic-like signature than burrowed dysaerobic facies.

# 4.3 SULPHUR/CARBON PLOTS

In normal marine environments iron sulphide production is controlled by the availability of organic matter whilst sulphate/ hydrogen sulphide are usually unlimited (Goldhaber and Kaplan, 1975; Jørgensen, 1977; Boudreau and Canfield, 1988). There tends to be a positive correlation between organic carbon and pyrite sulphur with a gradient of around 0.4 and a zero intercept (Berner, 1970; Goldhaber and Kaplan, 1974; Fig. 4.4). As organic matter must be destroyed for iron sulphide formation it is not immediately apparent why plots of pyrite sulphur and organic carbon should show a positive correlation. It may be that the oxidation of a constant fraction of the organic carbon, presumably the most metabolizable portion, is responsible for the correlation (Leventhal, 1983; Berner and Raiswell, 1983). This suggests that the original organic matter input to the sediment is heterogeneous with both reactive (hydrogen-rich) and refractory (hydrogenpoor) components.

In sediments in which all the organic matter is of homogenous composition a negative S/C correlation might be expected. For example, in their study of organic-rich limestones Boreham and Powey (1987) discovered a negative correlation between pyrite sulphur and organic carbon. In this case the organic carbon input was entirely from marine organic matter and all the organic carbon was involved in pyrite formation rather than a constant fraction of it.

Sulphate is not limiting to pyrite formation until concentrations reach very low values (Boudreau and

ENVIRONMENT	EUXINIC	ANOXIC	DYSOXIC			OXIC	
BIOFACIES ORBs	1	2	3	4	5	6	
PYRITE	abundant framboids and minute crystals of pyrite				pyrite only	fills voids	little or no pyrite
S ISOTOPES OF PYRITE	light to heavy S isotopes			only light isotopes			
DOP	1.0	0.	75			0	·5
Ua (ppm)	l	5 I	l 0 		[ 5? [		2
V/(V + Ni) whole rock	1.0 0.	83 0	·57			0	-46 
V/(V + Ni) porphyrins	1.0		).5 			(	)·4

Fig. 4.3. Proposed relationship between the palaeoecologically defined oxygen-restricted biofacies (ORBs) and geochemical phenomena.  $U_a$  values are those measured in British Jurassic mudrocks (e.g. Wignall and Myers, 1988). V/(V + Ni) boundaries show considerable overlap in their range according to Hatch and Leventhal (1992). The precise position of all the boundaries is somewhat tentative as there has been little attempt to integrate such geochemical data with palaeoecological information, with the exception of  $U_a$ .



Fig. 4.4. Sulphur/carbon plot showing fields typical of specific environments.

Westrich, 1984) and only in fresh or slightly brackish conditions is a distinctive signature of high organic carbon values and low pyrite sulphur values produced (Berner and Raiswell, 1984; Fig. 4.4).

In euxinic environments, hydrogen sulphide is present within the water column and iron sulphides form and settle from the water column (Berner and Raiswell, 1983). Leventhal (1983), in his study of the Black Sea, the type euxinic basin, showed that S/C plots have a similar positive slope to normal marine sediments but with a positive intercept on the S axis (Fig. 4.4). This he attributed to the addition of syngenetic pyrite formed in the water column, to the organic carbon-limited diagenetic pyrite. Essentially the most diagnostic feature of the euxinic S/C plot is the occurrence of high pyrite sulphur values at low organic carbon values.

By the mid-1980s S/C plots had been shown to be one of the most valuable geochemical indices for determining both palaeosalinity and palaeo-oxygen values. Several studies have apparently verified this utility (Raiswell and Berner, 1985; Leventhal, 1987; Leeder *et al.*, 1990; Maynard *et al.*, 1991). Unfortunately much subsequent study has shown that this approach is a good deal more limited than previously thought.

A significant proportion of organic carbon is lost from sediments during thermal maturation for which corrections must be made before S/C plots can be interpreted (Raiswell and Berner, 1987). More seriously for these interpretations, freshwater values have been obtained from marine sediments in which prolonged oxic reworking removes most pyrite before burial (Aller *et al.*, 1986). High salinities can also limit sulphate-reducing bacteria and thus produce S/C ratios more akin to freshwater (Sheu, 1987). Davis *et al.* (1988) have similarly challenged palaeosalinity interpretations, arguing that organic matter type and reactive iron content are of overriding importance in pyrite formation and neither are necessarily related to salinity variations.

Nonetheless S/C plots still have utility in identifying ancient euxinic environments where the characteristic feature of iron-limited pyrite formation is recorded as high sulphur and low carbon values. However, such euxinic sediments may not show a positive S/C plot as recent re-examination of Black Sea sediments shows no clearly defined positive correlation (Calvert and Karlin, 1991; Lyons and Berner, 1992).

It would appear that at least six factors control the formation of pyrite and affect S/C ratios:

(1) Sedimentation rate. In marine conditions low sedimentation rates beneath oxic bottom waters can lead to prolonged reworking of organic matter so that, ultimately, only unreactive material remains. Little sulphide is therefore generated in the SRZ and the resultant low S/C values are similar to those found in 'freshwater' conditions.

(2) The proportion of metabolizable organic carbon. Note that, prior to the Devonian, there was no terrigenous organic carbon component and the reactive component of the organic carbon was presumably much higher.

(3) Reactive (reducible) iron. Carbonate sediments in particular contain little iron and therefore little pyrite is formed unless euxinic conditions occur.

(4) Redox conditions of the bottom waters.

(5) Organic matter maturity. Correction must be made for organic carbon loss during burial.

(6) Sulphate concentration. This only appears important at very low or very high salinities.

In many studies, too many of these factors are unconstrained for conclusive palaeoenvironmental interpretations to be derived from S/C plots.

### 4.4 DEGREE OF PYRITIZATION

Despite the range of controls on pyrite formation, meaningful palaeoenvironmental information can be derived from consideration of the proportion of reactive iron in the sediment that is incorporated in pyrite (Raiswell and Berner. 1985). This is the degree of pyritization of iron (DOP) defined as:  $DOP = \frac{pyritic iron}{pyritic iron + acid soluble Fe}$ 

Under persistently anoxic conditions virtually all reactive iron reacts to form pyrite and DOP values generally exceed 0.75 (Raiswell *et al.*, 1988). Dysoxic settings tend to produce values ranging between 0.5 and 0.75, whilst little pyrite is preserved in oxic settings and DOP values are consequently low (Fig. 4.3). The DOP index is one of the few geochemical indices of palaeoenvironment which has been correlated and corroborated by palaeoecological data (Raiswell *et al.*, 1988).

The importance of sedimentation rates to DOP has yet to be fully evaluated (Raiswell, personal communication). Iron oxides and oxyhydroxides react rapidly and are unlikely to be rate affected but iron bound in clay minerals is much slower to react. If clay mineral iron is included within the reactive iron component then DOP will presumably increase with declining sedimentation rate (cf. Canfield *et al.*, 1992).

# 4.5 TRACE METALS

Black shales are frequently enriched relative to normal shales in a host of metals, particularly silver, molybdenum, zinc, nickel, copper, chromium, and vanadium and frequently uranium (Goldschmidt, 1954; Vine and Tourtelot, 1970). This reflects the unusual nature of black shale deposition, although the precise processes involved are only partially or poorly understood. The relative enrichment of trace metals varies greatly between black shales, presumably reflecting variations in the original environment such as sedimentation rate and porewater pH (e.g. Coveney et al., 1991), although these too have yet to be fully understood. Nonetheless several trace metal ratios have been proposed as measures of palaeoredox conditions (e.g. Hallberg, 1976; Dypvik, 1984; Dill, 1986; Jones and Manning, in press).

For most trace metals, their enrichment appears to be directly related to the anoxic conditions of black shale deposition. The process of enrichment are thought to be due to:

(1) precipitation as a sulphide;

(2) incorporation as a trace element in pyrite, the most ubiquitous authigenic sulphide;

(3) complexation with organic matter.

The majority of trace metals show a positive correlation when plotted against organic carbon, implying that the third factor is dominant (Vine and Tourtelot, 1970; Bralower and Thierstein, 1987). However, this may only reflect that organic matter preservation and metal enrichment are controlled by the anoxic depositional environment rather than there being any more direct relationship between them (Brumsack, 1980). Positive correlation with sulphur can similarly be held as evidence, albeit not definitive, for trace metal association with sulphides.

Arsenic, silver, cadmium, cobalt, zinc, mercury, and copper all appear to be closely associated with sulphides, most likely pyrite, in many black shales (Raiswell and Plant, 1980; Brumsack, 1989; Huerta-Diaz and Morse, 1992). Lead has also been suggested to be located in pyrite (Spears and Amin, 1981) although a significant proportion is probably formed as an end product in the uranium decay series. Much sulphide formation occurs in the surficial sediments where metals are supplied by diffusion from the overlying waters. Thus, sulphide formation and trace metal enrichment is favoured under slow sedimentation rates.

# 4.5.1 Molybdenum

Mo is one of the most abundant trace metals in the modern oceans where it occurs at concentrations of 10 ppb (Brumsack, 1989), and it is also one of the most common and most highly enriched trace metals in black shales (Coveney and Martin, 1983; Pevear and Grabowski, 1985). Vine and Tourtelot (1970) noted the correlation of Mo with organic carbon but little Mo is present in modern marine plankton (Pilipchuk and Volkov, 1974; Brumsack, 1989). Brumsack (1989) suggested that Mo is initially adsorbed onto humic substances in the reduced Mo<sup>5+</sup> state but that it is ultimately precipitated as a sulphide, possibly a trace element in pyrite (Huerta-Diaz and Morse, 1992). Jacobs et al. (1987) have documented co-precipitation of Mo with FeS in the modern anoxic setting of the Carioco Trench. In the Pennsylvanian Mecca Quarry (black) Shale, there is a considerable variation in the degree of Mo enrichment with nearer-shore black shales overlying coals having the greatest enrichment, in excess of 1000 ppm (Coveney and Martin, 1983; Coveney et al., 1991). Coveney and his co-workers attribute this to adsorption onto humic organic matter under acidic conditions. This conclusion is in agreement with Brumsack (1989) but not with observations from recent environments (Jacobs et al., 1987; Huerta-Diaz and Morse, 1992).

#### 4.5.2 Vanadium and nickel

The sedimentary geochemistry of vanadium and nickel are closely similar (Lewan and Maynard, 1982) although subtle variations in their chemistry can give useful palaeoenvironmental information. Vine and Tourtelot (1970) noted that V is concentrated by tunicates (sea squirts) and that enriched values in black shales could be due to enhanced preservation of such organisms. However, tunicates are sessile, benthic organisms which are highly unlikely to occur in oxygenpoor black shale environments.

Both Ni and V appear to be concentrated in tetrapyle complexes (porphyrins), derived from chlorophyll, which are preferentially preserved under anoxic conditions (Lewan and Maynard, 1982; Dill, 1986). The vanadyl (V(IV)) cation is most stable under reducing acidic conditions, typical of euxinic basins; the solubility of Ni is not influenced by the redox potential (Jacobs et al., 1985) but, under anoxic conditions, the greater availability of hydrogen sulphide causes nickel sulphide formation (Lewan and Maynard, 1982; Repeta et al., 1992). Therefore the V/(V + Ni) values of porphyrins from euxinic environments are generally greater than 0.5 (Lewan, 1984). Under dysoxic conditions Ni more readily complexes with organic matter and the V/(V + Ni) ratio is generally less than 0.5. Under very alkaline conditions, typical of some lakes, V is not available for metallation and the V/(V + Ni) falls below 0.1 (Lewan, 1984). V can also be encountered in silicates (Dill, 1986) as the vanadyl ion is readily adsorbed by clay particle surfaces when it is reduced to V(III) during burial (Breit and Wanty, 1991). Therefore the absolute values of the V/(V + Ni) ratio given by Lewan (1984) for porphyrins may differ from whole rock values which could include V associated with clay minerals. This probably explains the slight discrepancy in the values quoted by Hatch and Leventhal (1992) for measuring an oxygen gradient (Fig. 4.3) as their values were derived from whole rock samples.

Dill (1986) proposed the V/Cr index as a measure of palaeoredox conditions. Chromium is entirely of detrital origin and it should not therefore fluctuate with redox conditions. V/Cr values in excess of 2 apparently indicate anoxic conditions whilst values less than 1 indicate normal oxic conditions (Dill, 1986). Similarly, Dypvik (1984) suggested that Ni/Co ratios may also reflect oxygen levels; high values being diagnostic of anoxia. It would be useful to independently assess these ratios using palaeoecological data to confirm their validity.

#### 4.5.3 Manganese

Manganese sulphide is highly soluble and so is not encountered in black shales although, under highly reducing conditions, Mn can occur as a trace element in pyrite (Huerta-Diaz and Morse, 1992). However, Mn carbonates are commonly encountered in close stratigraphic association with black shales and they may even occur finely interbedded with organic-rich shales (e.g. Jenkyns et al., 1991). Manganese carbonate precipitates in the denitrification zone (cf. Section 4.1.2) whilst it occurs in solution in the more intensely anoxic conditions of sulphate reduction. Thus, in a euxinic basin peak dissolved Mn concentrations occur around the anoxic/oxic boundary and, if this interface remains stable over geological time, then a 'bath-tub ring' of Mn carbonates may encircle areas of black shale deposition (Frakes and Bolton, 1984; Force and Cannon, 1988). Alternatively, fluctuating redox conditions will produce interbedded black shales and Mn carbonates (Jenkyns et al., 1991).

#### 4.5.4 Rare earth elements

The rare earth elements (REE) are present in trace amounts in the world's oceans. The majority of these elements occur in the soluble 3+ oxidation state but cerium occurs as either Ce<sup>3+</sup> or Ce<sup>4+</sup> depending on the redox chemistry (Wright *et al.*, 1984). In oxic oceans, Ce<sup>4+</sup> is precipated with iron oxyhydroxides thus producing a negative Ce anomaly in REE abundance plots (Holser *et al.*, 1986; Elderfield, 1988). In anoxic oceans the Ce<sup>3+</sup> cation is stable and remains in solution and there is no corresponding Ce anomaly. REEs have such a long residence time in the world's oceans that they have a uniform global signature which reflects the oceanic redox chemistry. Only semi-isolated basins like the Black Sea have their own distinctive REE abundance pattern (Elderfield, 1988).

Wright et al. (1984) have demonstrated that biogenic apatite concentrates REE whilst faithfully recording the oceanic REE pattern. Thus, by analysing REEs in conodont apatite and in fish bones they recorded changes in the redox conditions of the oceans through the Phanerozoic. This reveals that, from the Cambrian to the Silurian and during the Early Triassic most of the world's oceans were anoxic. In addition to analysing secular global trends, REE patterns have the additional potential of detecting the degree of isolation of basin waters from the world's oceans.

#### 4.5.5 Uranium

Like many other trace metals, uranium is commonly enriched in black shales (Swanson, 1960). and concentrations can reach 200 ppm which is sufficient to cause extensive radiation damage to organic matter (Sundararaman and Dahl, 1993). In recent years our knowledge of U distribution in shales has advanced considerably due to the advent of field-portable gamma-ray spectrometers which allow the rapid acquisition of large data sets (Myers and Wignall, 1987).

Potassium, thorium, and uranium are the three most common naturally occurring radioactive elements and, by measuring the energy and intensity of their gammaray emissions, their abundance can be measured with a gamma-ray spectrometer (Myers and Wignall, 1987).

Most shales have measurable concentrations of K, Th, and U contained mainly in their clay fraction and also in accessory minerals. However, under anoxic depositional conditions U appears to precipitated as an authigenic element (see below). It is therefore desirable to know what proportion of the U measured by the gamma-ray spectrometer ( $U_{total}$ ) consists of authigenic uranium ( $U_a$ ) and what of detrital uranium ( $U_{det}$ ). In most marine shales deposited under normal, oxic conditions, Th/ $U_{det}$  ratios generally range between 3 to 5, close to crustal values. No authigenic enrichment occurs under such conditions but in anoxic conditions the measured U value can be expressed as:

$$U_{total} = U_{det} + U_a.$$

No corresponding authigenic enrichment of Th occurs under anoxic conditions and  $U_{det}$  can be given by:

$$U_{det} = Th/3$$

allowing the authigenic U component to be calculated from:

$$U_a = U_{total} - Th/3$$
.

Using this calculation it has been possible to assess relative changes of palaeo-oxygen levels in British Jurassic mudrocks (Myers and Wignall, 1987; Wignall and Myers, 1988) and Carboniferous mudrocks (Maynard *et al.*, 1991; Wignall and Maynard, 1993). The calculation is only valid for fine-grained terrigenous strata deposited under marine conditions. Th/U ratios of carbonate-rich rocks are poorly known and  $U_a$ cannot therefore be calculated, although, in pure carbonates, all the U should be of authigenic origin in the absence of any detrital component.

Comparison of  $U_a$  values with palaeoecological indices of palaeo-oxygen levels (e.g. Fig. 3.8) reveals that  $U_a$  enrichment is a subtle indicator of benthic redox conditions; this was first seen in the data of Knowles (1964). Unlike several other geochemical indices, it appears to be particularly useful for distinguishing between dysaerobic facies (Fig. 4.3). For British Jurassic black shales,  $U_a$  values around 2 ppm occur in sediments with uppermost dysaerobic faunas (ORB 6; cf. Wignall, 1990a), whilst values in excess of 10 ppm are generally associated with ORBs 1, 2, and 3 (Fig. 4.3). In the Carboniferous the absolute values of  $U_a$  associated with any particular ORB are different but the relationship remains the same; anaerobic sediments are more enriched in  $U_a$  than dysaerobic examples.

Gamma-ray spectrometry data are also available from boreholes, therefore  $U_a$  calculation is one of the most widely available means for palaeoenvironmental assessment of black shales. However, the theoretical basis behind authigenic U enrichment is only partially understood.

In oxic waters, where pH is around 7 or greater, U occurs as a soluble, stable uranyl  $(U^{6+})$  carbonate complex UO<sub>2</sub>(CO<sub>3</sub>)<sup>4--</sup> (Langmuir, 1978). Around the redox boundary U occurs as the highly soluble uranyl ion  $UO_2^+$ , whilst in anoxic waters, at pH values of 7 or less, it forms much less soluble uranous (U<sup>++</sup>) fluoride complexes (Langmuir, 1979). Borovec et al. (1978) demonstrated that U can be fixed in anoxic sediments following sorption of uranyl ions by humic acids. This may explain the well documented positive correlation of U and organic matter (Swanson, 1960; Leventhal, 1981), particularly with terrestrial organic matter with its high proportion of cellulose and lignin. Many Pennsylvanian black shales of the United States show peak U values in nearshore settings where humic organic matter is predominant and lesser values in more distal, sapropelic black shales (Coveney et al., 1991). A similar distribution is seen in a Namurian black shale from northern England (Fig. 4.5).

Studies of U in modern anoxic environments indicate that the humic acid/uranyl ion reaction fails to account for the observed distributions. In Saanich Inlet, where anoxic, H<sub>2</sub>S-bearing water occurs in the lower water column, there is only a slight decline in dissolved U values across the redox boundary suggesting that there is no wholesale reduction and precipitation of U and that U(VI) is kinetically stable in anoxic waters (Anderson et al., 1989a). Uranium flux to the sediments is greatest during the spring plankton bloom suggesting that non-humic organic matter can also fix U, but this flux accounts for only a small fraction of the U burial flux. Similarly, in the Black Sea, the particulate U. flux to the sediment is two orders of magnitude less than the burial flux indicating that most U fixation must occur by diffusion into the sediment and/or reactions at the sediment surface (Anderson et al., 1989b; Barnes and Cochran, 1990). Thus U<sub>a</sub> fixation must be dependent on the sedimentation rate to some extent.

Permanent porewater anoxia is required for U fixation because, as demonstrated by Anderson *et al.* (1989a), only 2 to 3 minutes' oxidation is required to increase porewater dissolved U concentration by a



**Fig. 4.5.** Contoured U<sub>a</sub> values from the black shale associated with the *Gastrioceras cumbriense* Marine Band from the Late Carboniferous of northern England. Lowest values occur in the basin centre and increase towards the margins, probably due to the increase in the proportion of humic organic matter (from Wignall and Maynard, 1993).

factor of 6, presumably due to the rapid production of the uranyl ion. This is clear evidence that black shales with enriched  $U_a$  values accumulated during prolonged anoxic periods. Therefore poikiloaerobic rather than dysaerobic sediments should have higher  $U_a$  concentrations.

Despite the good correlation between organic carbon and  $U_a$  (e.g. Fig. 4.6) and the known relationship between humic acids and uranyl ions, there is little petrographic evidence to support their close relationship. By utilizing autoradiography, Knowles (1964) observed that U was preferentially concentrated in francolite. Fine-grained francolite in particular, with its greater surface area, appears to be particularly good at scavenging U (Q. Fisher, personal communication). Pevear and Grabowski (1985) noted that U is concentrated in bone-rich horizons, but conversely, Coveney (1985) documents an inverse correlation between phosphorus and U.

In summary, three main factors appear responsible for  $U_a$  enrichment:

- (1) the intensity and duration of benthic anoxia;
- (2) the abundance of the component in which U is



**Fig. 4.6.** Plot of U<sub>a</sub> and U<sub>tot</sub> against organic carbon from the Jet Rock (Toarcian, Lower Jurassic) at Port Mulgrave, north Yorkshire. Whilst there is a reasonably good positive correlation between authigenic U and TOC, the total U values show little relationship, presumably because variations in the detrital input of U are unrelated to the conditions which lead to organic carbon preservation.

concentrated. This is poorly known although both humic organic matter and francolite are contenders;

(3) the sedimentation rate.

As there is good empirical evidence for the relationship between  $U_a$  and the first factor (e.g. Wignall and Myers, 1988), it is probable that both the second and third factors covary with the first. Indeed, Mangini and Dominik (1979) have utilized U isotope ratios from a sequence of Late Quaternary mudrocks from the eastern Mediterranean, to demonstrate that black shale sedimentation rates in this sequence are twice as slow as the background rates. Plots of  $U_a$  can therefore be used as a measure of changing bottom-water redox conditions, although the absolute magnitude of enrichment is controlled by several factors.

Analysis of  $U_a$  and other geochemical indices can therefore provide valuable clues to shale depositional environments (Fig. 4.3). Further increases in their utility will come from integrated geochemical and palaeoecological studies. Considerable further work is also required to evaluate the nature of trace metal enrichment in anoxic conditions.

Black shales may occasionally have sufficient concentrations of trace metals to be worth exploiting. However, syngenetic processes on their own are unlikely to cause sufficient metal enrichment to produce ores, and such stratiform deposits only tend to form in thin black shales that cap more permeable strata. Enrichment is caused in these cases by precipitation of metals from groundwaters at the base of black shales which commonly mark a sharp redox boundary (Brongersma-Sanders, 1965; Schmitz, 1985).

As most syngenetic trace metal enrichment processes are rate dependent, low sedimentation rates combined with anoxic bottom waters tend to favour their accumulation. Brumsack (1989) has utilized this phenomenon to distinguish between the Gulf of California, where anoxia is caused by high productivity, and the Black Sea, where productivity is moderately low but organic matter is well preserved in anoxic conditions. Cadmium, silver, zinc, and copper are bound to highly labile organic matter but, in the Gulf of California, high sedimentation rates and intense recycling of organic matter ensures that there is little enrichment of these elements in the sediment. Conversely the low sedimentation rates and enhanced preservation of organic matter in the Black Sea favours trace metal enrichment in the sediment. Trace metal enrichment patterns of many ancient black shales are comparable with those of the Black Sea (Brumsack, 1980, 1991; Bralower and Thierstein, 1987).

# Organic geochemistry

# 5.1 INTRODUCTION

The organic matter of black shales is derived from a variety of different sources, principally lipid-rich phytoplankton and bacteria and humic terrigenous organic matter. Study of this organic component is important for the assessment of source rock maturation and the correlation between source rocks and migrated oils. However this chapter is specifically focused on the use of organic geochemical data for palaeoenvironmental analysis.

Organic matter analysis falls into three main categories:

(1) Bulk chemical analysis of the total organic matter of the rock and its carbon isotope ratios.

(2) Petrographic investigation of the palynomorphs and kerogen macerals.

(3) Investigation of specific biological marker molecules (biomarkers) identified in the soluble component (bitumen) of the organic matter

### 5.2 BULK CHEMICAL ANALYSIS

#### 5.2.1 Van Krevelen diagrams

The characterization of organic matter on a van Krevelen diagram is arguably the single most informative method of analysis of black shales for it supplies information on both the type and maturity of the organic matter content of the rock (Tissot and Welte, 1978; Pratt *et al.*, 1986; Jones, 1987). The van Krevelen diagram, as originally designed for use in black shale analysis (Tissot *et al.*, 1974), plots the atomic H/C and O/C ratios of kerogens. For immature rocks, three main kerogen types are known:

**Type I kerogen:** This rare hydrogen-rich, oxygenpoor kerogen type has excellent potential for oil generation, producing distinctive aromatic-poor oils (Katz, 1988). The type example, from the Eocene, Green River Formation of Colorado, is thought to be derived solely from algal organic matter (cf. Section 8.3).

Type II kerogen: The vast majority of the world's marine petroleum source rocks contain Type II kerogen

which is supposedly derived from bacterially altered marine organic matter, such as phytoplantkton, with a minor component of terrigenous organic matter (TOM). However some terrigenous plant material such as leaves and spores are also lipid rich and may therefore contribute substantially to some Type II kerogens. Type II-sourced oils are rich in naphthene and aromatic hydrocarbons.

**Type III kerogen:** Characterized by low H/C ratios and generally high O/C values, Type III kerogen has a composition close to that of woody organic matter which is thought to be the main contributing source (Tissot and Welte, 1978). Due to the low oxygen demand of such material, Type III kerogen can accumulate under oxic and upper dysoxic conditions; the preservation of Types I and II is thought to require anoxic/suboxic conditions.

#### 5.2.2 Modified van Krevelen diagrams

With the development of the Rock-Eval pyrolysis technique (Espitalie *et al.*, 1977) it became possible to rapidly and cheaply assess black shales using a modified van Krevelen plot (Fig. 5.1). This plots the Hydrogen Index or HI ( $S_1$ /TOC) against the oxygen index or OI ( $S_2$ /TOC), where  $S_1$  is the amount of volatilized free organic compounds and  $S_2$  the amount of organic compounds released by thermal cracking of kerogen between 250 °C and 550 °C.

Tissot (1984) has added a fourth kerogen type to the modified plot, characterized by very low HI values and high OI values. **Type IV kerogen** consists of highly reworked organic matter which has been extensively  $\pi$ . Judified and has no hydrocarbon generative potential.

#### 5.2.3 Organic facies

In an attempt to relate the depositional environment and generative potential of black shales to pyrolysis data, Jones (1984, 1987) devised a spectrum of organic facies based primarily on HI values (Fig. 5.2). An organic facies is defined as, 'a mappable rock unit, distinguishable from adjacent rock units by the character of its organic matter without regard to the inorganic aspects of the sediment' (Jones, 1984, p. 163). Only organic facies A, AB, and B are encountered in black



Fig. 5.1. Modified van Krevelen diagram derived from Rock-Eval data, with Types I, II, and III kerogens delineated. Data points show the relationship between biofacies and kerogen type from the mid-Cretaceous Greenhorn Formation (from Pratt, 1984).

shales, the remaining facies are found in a variety of normal marine and terrestrial facies.

Organic facies A consists of exceptionally hydrogenrich organic matter thought to be entirely sourced by algal matter, although petrographic analysis shows that amorphous organic matter is usually the dominant maceral. Organic facies A is very rare because no TOM input is required for its formation; only in exceptionally arid conditions or in the early Palaeozoic, before the evolution of land plants, is this condition met.

Organic facies AB consists mostly of algal and bacterial organic matter with a minor proportion of TOM. It is commonly associated with transgressive black shales.

Organic facies B is the most common facies type encountered in black shales. Algae, bacteria, and a minor, but significant, component of TOM constitute the heterogeneous organic matter sources.



Fig. 5.2. Organic facies of Jones (1987) as defined on a modified van Krevelen plot.

The organic facies concept is a valuable one for it combines both Rock-Eval and petrographic data. It would be useful to compare the facies with the oxygenrestricted biofacies defined in Chapter 3. The utility of Rock-Eval data for palaeoenvironmental analysis is demonstrated in the study of Baudin *et al.* (1989) on the organic facies of Toarcian sediments of Europe (Fig. 5.3). This clearly demonstrates the restriction of the most organic-rich Type II sediments to basin centres with a 'bull's-eye' pattern of increasingly more organicpoor, less generative facies surrounding them.

However, problems exist in the interpretation and use of van Krevelen diagrams (Katz, 1983). In particular, the depositional environment can exert a strong control on not only the type of organic matter, but also its apparent maturity (Pratt, 1984; Pratt *et al.*, 1986; Pasley *et al.*, 1991). Pratt (1984) has shown, for the Cretaceous Greenhorn Formation of the US mid-West, that the transition from anaerobic to dysaerobic to aerobic strata is marked by a corresponding change from Types I to II to III kerogen (Fig. 5.1). This does not record a change in the organic matter input but rather it reflects gradually deteriorating preservation of the marine organic matter precursor (Pratt, 1984). Thus



Fig. 5.3. Palaeogeographical map of the Toarcian of the northern hemisphere showing distribution of kerogen types. The best developed source rocks (Type II kerogen, high TOC) are found in local depocentres in France, Germany, and northern England. Reproduced from Baudin *et al.* (1989) with the authors' permission.

Type III kerogen can have two distinct origins: degraded marine organic matter or pristine terrigenous organic matter. Distinguishing between these two different origins requires maceral analysis as it is not readily achieved using Rock-Eval pyrolysis (Tyson, 1989).

# 5.3 MACERAL AND PALYNOMORPH ANALYSIS

# 5.3.1 Macerals

Although not a geochemical technique itself, the visual indentification of kerogen particles (macerals) in thin

section or smear slides can provide an independent means of determining the source of organic matter and corroborating bulk organic geochemical analyses.

Several similar classification schemes are available for the description of kerogen macerals in thin section (e.g. Waples, 1985). The scheme of Hutton *et al.* (1980) is summarized in Figure 5.4. All classifications distinguish between oxidized, carbon-rich matter (inertinite), humic organic matter (vitrinite), and the lipid-rich particles of membranous material (exinite) or amorphous organic matter (liptinite) (Brooks *et al.*, 1987). The origin of liptinite is uncertain, but it may be the product of algal or fungal attack on other macerals. The several varieties of exinite are typically associated



Fig. 5.4. Maceral classification scheme of Hutton et al. (1980) derived from petrographic analysis and its relationship to kerogen types.

with Types I and II kerogen and their origin can commonly be identified. Alginite macerals of algal origin are common in many black shales of which Hutton *et al.* (1980) distinguishes two types (A and B) on the basis of their size.

#### 5.3.2 Palynomorphs

Palynomorphs, such as spores, pollen, dinoflagellate cysts, and acritarchs, can be analysed by transmitted light microscopy of acid-insoluble residues. The results can provide further useful information on organic matter sources. Palynomorphs rarely constitute more than 10% of organic residues (Tyson, 1989). The remaining material consists of a variety of kerogen particles that can be directly equated with kerogen macerals seen in thin section (cf. Table 2 of Tyson, 1989). Hart (1986) has proposed a classification scheme relating kerogens to their precursor matter (e.g. phytoclasts, scleratoclasts, protistoclasts) and their degree of degradation. However, many kerogen particles are classified as amorphous organic matter (AOM),

sometimes called amorphogen, probably the equivalent of liptinite, which Ebukanson and Kinghorn (1985) described as, 'unorganized fluffy to semi-coherent masses.' In a quantified palynological analysis, Tyson (1989) identified several varieties of AOM and distinguished source-environment variations on a series of ternary AOM-exinite-phytoclast plots. However, the uncertain origin of AOM is one of the main drawbacks in deducing palaeoenvironmental interpretations from palynological analysis alone (Jones, 1987).

The phycoma stage of prasinophycean algae is commonly abundant in black shale palynological samples. Tyson (1989) suggests that they are indicative of a stable, stratified water column whilst several other authors have suggested that they are indicative of brackish surface waters (Riegal *et al.*, 1986; Prauss and Riegal, 1989; Prauss *et al.*, 1991). The modern ecological preferences of prasinophyceans are very poorly known, but there is little support from geological evidence to indicate a preference for low salinity. For example, Prauss *et al.* (1991) suggested that the presence of prasinophytes in the Posidonia Shale of Southern Germany is evidence for accumulation beneath low salinity surface waters. However, the presence of a diverse, stenohaline nektonic fauna of marine reptiles, fish and ammonites in the shales suggests that the surface waters were probably of normal salinity.

# 5.4 CARBON ISOTOPES ( $\delta^{13}$ C)

In a pioneering study, Newman et al. (1973) demonstrated that carbon isotopes could be used to distinguish between marine and terrigenous organic matter in Quaternary cores. Modern marine organic matter has  $\delta^{13}$ C values ranging between -20% and -25% whilst TOM is lighter, ranging between -23%and -33%; -30% is a typical value for many land plants (Dean et al., 1986; Weissert, 1989). Carbon isotope analysis of kerogen was therefore shown to be useful for distinguishing sources of organic matter. However, the picture has become considerably more complicated due to apparent secular changes in  $\delta^{13}C$ values. During the Cretaceous the relative values of  $\delta^{13}C$  were reversed with values of marine organic matter (at -26% to -28%) being lighter than contemporary TOM (Dean et al., 1986). Several carbon isotope studies on the Jurassic Posidonia Shale of southern Germany have shown that yet further factors may influence kerogen  $\delta^{13}$ C values.

Values of  $\delta^{13}$ C in Posidonia Shales kerogens are considerably lighter than those in shales both above and below this formation (Kuspert, 1982; Jenkyns and Clayton, 1986). A 'traditional' interpretation of this observation would be that there was increase in the proportion of TOM in the Posidonia Shale, but this is neither supported by Rock-Eval or petrographic data as these show that the proportion of marine organic matter reaches its peak in the isotopically lightest horizons (Kuspert, 1982; Prauss et al., 1991). Kuspert (1982) interpreted his data to indicate reworking of more abundant organic matter in the lower water column during formation of the Posidonia Shale. This caused preferential oxidation of isotopically light carbon which was then re-incorporated into the plankton biomass. Moldowan et al. (1986) adopted Kuspert's model and showed a distinct negative correlation between HI and  $\delta^{13}$ C (compare with the Greifen model discussed in Section 6.4.1). Alternatively, Jenkyns and Clayton (1986) suggested that the light values reflected enhanced preservation during the peak of black shale formation. Pratt et al. (1986) have demonstrated a similar phenomenon in Cretaceous black shales where lipids derived from marine organic matter in anaerobic strata are 1.9‰ lighter than lipids from a

similar source in dysaerobic/aerobic strata. McArthur et al. (1992) have also noted that prolonged oxic degradation of organic matter can change  $\delta^{13}$ C values by up to 2.5‰. However, in the Posidonia Shale  $\delta^{13}$ C values are as light as -33% (Jenkyns and Clayton, 1986) and the magnitude of the depletion is probably too great to be explained by preservational variations alone.

A further explanation for the carbon isotope variations in the Posidonia Shale may be derived from the changing nature of the planktonic populations. The palynomorph analyses of Prauss *et al.* (1991) have revealed several types of planktonic input into the Posidonia Shale. The most organic-rich intervals contain common algal bodies of a *Botryococcus*-like genus—the isotopically light values may be accounted for if this organism fractionated particularly <sup>13</sup>C-poor organic matter (Jenkyns and Clayton, 1986; Prauss *et al.*, 1991).

Clearly,  $\delta^{13}$ C values can only be used for diagnosing organic matter types with great care because several other factors, including preservational quality and the vital effects of some organisms, are important. The effect of temperature variation, although commonly overlooked, may also be significant (de Boer, 1982). Further understanding of black shale depositional conditions from  $\delta^{13}$ C values may be attained from the carbon isotope signal of individual organic molecules rather than from the currently used values which are derived from the entire organic fraction of rocks (Hayes *et al.*, 1989; Bjoroy *et al.*, 1991).

# 5.5 BIOMARKERS

The preceding sections have outlined the use of organic geochemistry in palaeoenvironmental assessment based on bulk analysis of the organic component of rocks. In sharp contrast biomaker analysis involves the detection of specific organic molecules that may constitute less than 1% of the total organic matter content of the rock (Mackenzie, 1984).

Biomarkers are 'sedimentary organic compounds whose basic skeleton suggests an unambiguous link with known contemporary products, and [which] were synthesised by biota present at the time of deposition of the sediment' (Kohnen *et al.*, 1991, p. 775). The majority of biomarkers belong to the porphyrins, triterpenoids, steroids, hopanoids, and acyclic isoprenoids which, unlike most organic molecules. do not appear to be modified beyond recognition during burial (Mackenzie, 1984; Brassell, 1992).

Biomarkers have principally been used in the study of

biodegradation and maturation of source rocks and the correlation and migration of oils, although their lesser role, of palaeoenvironmental interpretation, is highlighted here despite the opinion of Mackenzie (1984, p. 180) that it is 'a distant aim of biological marker organic geochemistry to be able to predict the detailed lipid composition of a sediment at the time of its deposition'.

A diverse range of biomarkers have now been determined, of which the majority are used to distinguish between the principal sources of organic matter (Table 5.1). The rationale behind the use of biomarkers lies in the recognition of closely similar organic molecules in modern environments. Thus the  $C_{34}$  acyclic isoprenoid alkane botryococcane is only synthesized by the freshwater alga *Botryococcus braunii*. Therefore the presence of this molecule in bitumen points to a lacustrine depositional environment (Moldowan *et al.*, 1985). Similarly, coccolithophoroids are unique in secreting long-chain alkenones. These appear particularly resistant to degradation and they survive virtually unaltered in the geological record (Volkman, 1988).

As the above demonstrates, environmental applications of biomarkers are based on the presence or absence

 Table 5.1.
 List of some of the more commonly used and widely accepted biomarkers (e.g. Brassell, 1992).

#### Marine organic matter

*n*-alkanes and *n*-fatty acids with medium molecular weight  $(C_{12}-C_{20})$  and odd carbon chain length preference, particularly  $C_{15}$  and  $C_{17}$ .  $C_{15}-C_{20}$  isoprenoids. Ubiquitous triterpenoids (including hopanes). *Coccolithophoroids*: long-chain alkenones ( $C_{37}$  and  $C_{38}$  methyl ketones and  $C_{38}$  and  $C_{39}$  ethyl ketones). *Dionoflagellates*: 4-methyl steranes.

#### Terrigenous organic matter

*n*-alkanes with high molecular weight  $(C_{25}-C_{33})$  and odd chain length preferences even *n*-alkanoic acids in the  $C_{24}-C_{29}$  region. Steranes, with  $C_{29}$  dominant. Conifers and conifer resins: tri- and tetracyclic diterpanes.

#### Bacteria

Predominance of hopanes, with few *n*-alkanes. Cyanobacteria:  $C_{27}$ - $C_{35}$  pentacyclic triterpanes of the hopane

series.  $C_{32}$ - $C_{35}$  hopanoids. Sulphate-reducing bacteria:  $C_{26}$ - $C_{32}$  n-alkanes with even

ship hale -real ting but term.  $C_{26} - C_{32}$  h-alkales with even chain length preference.

Methanogenic bacteria: triterpanes, including lycophane, bisnorhopane and squalane (a  $C_{30}$  acyclic triterpane),  $C_{25}$  isoprenoid alkane, pentamethyleicosane.

#### Hypersaline environments

 $C_{16}$ - $C_{30}$  *n*-alkanes with even chain length preference. abbsteranes, hopenes, b-carotene, trimethyl dodecane.

of distinct molecules, more quantified biomarker analyses have so far met with little success. For example, Huang and Meinschein (1979) noted the strong correlation between sterols and depositional environment. They suggested that plankton-derived C27 sterols dominate in marine conditions, higher plants contain mostly  $C_{29}$  sterols and therefore characterize terrigenous facies, whilst lacustrine environments apparently have equal quantities of  $C_{27}$ ,  $C_{28}$ , and  $C_{29}$  sterols. Therefore, by plotting ternary composition diagrams of reduced sterols (steranes), Huang and Meinschein (1979) proposed that ancient environments could be determined. The validity of the empirically derived sterane plots has not withstood the test of further data (Volkman, 1988). Palacas et al. (1984) could derive no informative conclusions from sterane ratios in carbonate source rock and Moldowan et al. (1985) found that steranes from a wide range of sources showed considerable overlap.

Curiously, biomarkers have so far failed to provide a reliable index for detecting palaeo-oxygen values. An initially promising approach was suggested by Dydik et al. (1978) based on the proportions of the acyclic isoprenoids, pristane (tetramethylpentadecane) and phytane (tetramethylhexadecane). Dydik et al. (1978) traced the formation of these isoprenoids via a complex series of reactions involving the phytyl side-chain of chlorophyll. Pristane, it was suggested, arose via oxidation and decarboxylation of phytol. Conversely the dehydration and reduction of phytol resulted in phytane. Thus the pristane/phytane (Pr/Ph) ratio was considered to reflect the redox conditions of the depositional environment. High Pr/Ph ratios supposedly occurred in well oxygenated environments whilst low values, around 1.0 or less, indicated anoxic conditions and a good source rock. In their original analyses, Dydik et al. (1978) noted that the Pr/Ph ratio from the Posidonia Shale was 2.4, a high value indicating oxic conditions even though the remaining geological evidence indicates intensely anoxic conditions (Section 3.11). This value was attributed to the preferential production of pristane in a thermally mature sample. By implication, therefore, Pr/Ph ratios can only be safely used in the palaeoenvironmental analysis of relatively immature samples. Unfortunately recent developments have shown that the ratio is of even less utility than first proposed.

Pristane may also be derived from the tocophenols of zooplankton and so fluctuations in their flux to the sediment may also affect Pr/Ph ratios (Goossens *et al.*, 1984). Of even more importance, archaebacteria, such as the haloalkaliphilic bacteria, may be the source of much of the isoprenoids seen in bitumens (ten Haven *et* 

al., 1987). These bacteria are abundant in strongly reducing, hypersaline environments (Volkman, 1988). Therefore several authors suggested the use of Pr/Ph ratios as a measure of palaeosalinity (Mello et al., 1988; Powell, 1988). Ratios less than 1.0 supposedly indicate hypersalinity rather than intense anoxicity as originally proposed (Dydik et al., 1978). However, very low ratios are also associated with environments with very low ratios of terrigenous to marine organic matter, as encountered in carbonate facies (Moldowan et al., 1985). It is clearly unsatisifactory to use Pr/Ph ratios for their original designated purpose of measuring palaeooxygen levels (Pratt, 1984; ten Haven et al., 1987) and any other application is dubious given the plethora of sources and numerous factors controlling the relative abundance of isoprenoids.

More recently, Peters and Moldowan (1991) have suggested that a homohopane index may prove useful as a measure of palaeo-oxygen levels. Homohopanes are produced by the breakdown of bacterially derived polyhydroxyhopanoids.  $C_{31}$  to  $C_{34}$  homohopanes are formed by the oxidative cleavage of side chains followed by reduction whilst, in anoxic settings, the  $C_{35}$ homohopane is formed directly by the reduction of  $C_{35}$ homohopane to the sum of the total of the  $C_{31}$  to  $C_{35}$  homohopanes should increase as oxygen levels decrease (Peters and Moldowan, 1991).

Palaeoenvironmental inferences from biomarkers are only valid if there is only one, well-defined origin for each biomarker but commonly this is not the case. For example, the pentacyclic triterpenoid, gammercane was first recorded from the Eocene Green River Formation and it was assumed to be diagnostic of the unusual lacustrine conditions in which this source rock formed (Seifert and Moldowan, 1981; Section 8.3). However, gammercane is now thought to be a rather common bacterial product (Jones, 1987; Mello *et al.*, 1988). Biomarkers indicative of bacteria are of little use because bacterial alteration is ubiquitous and their biomarkers should be expected in all bitumens. Cyanobacteria biomarkers can, however, indicate deposition in the photic zone. The presence of TOM biomarkers in bitumen should also come as no surprise because a small amount of terrigenous plant material reaches even the most distal marine settings (Gagosian and Peltzer, 1986).

A further problem in biomarker interpretation lies in the unknown nature of organic compounds formed by extinct organisms. For example, Middle Ordovician bitumens contain abundant medium chain *n*-alkanes  $(C_{11}-C_{19})$  with odd chain length preference but no isoprenoids (Jacobson *et al.*, 1988). This strange signature is useful for characterizing Ordovician source rocks but the palaeoenvironmental significance is unknown. Perhaps the most fundamental question yet to be addressed in biomarker studies is whether such rare molecules truly record the nature of the original organic matter and therefore tell us something of the depositional environment.

In summary, Pratt *et al.* (1986, p. 68) are probably correct to consider that.

bulk properties of the organic matter (organic carbon content, hydrogen richness and  ${}^{13}C/{}^{12}C$  ratios) are more reliable indicators of depositional and early diagenetic conditions than ... abundances and ratios of biological marker compounds (biomarkers).

# Productivity versus preservation in black shale formation

# 6.1 ANOXIA AND ORGANIC MATTER PRESERVATION-CAUSE OR CONSEQUENCE?

The preceding chapters have been mostly concerned with detailing the numerous methods available for documenting palaeo-oxygen levels. There is overwhelming evidence that most black shales accumulated beneath dysoxic or anoxic water. Therefore the detection of such conditions is of paramount importance in any black shale/source rock study. However, whether this oxygen deficiency is a cause of organic matter preservation or merely a symptom of it is one of the most contentious issues in current black shale debates. As Hollander *et al.* (1992, p. 825) have succinctly noted, 'The central question in this controversy is whether the presence or absence of oxygen in bottom waters has any control on the accumulation of organic matter.'

Woolnough (1937) was amongst the first to suggest that organic carbon mineralization in anoxic conditions was less efficient than in oxic conditions and that organic-rich shales accumulate as a result of enhanced preservation in anoxic environments. This preservation model has received widespread support (e.g. Demaison and Moore, 1980; Funnell, 1987; Tyson, 1987; Canfield, 1989a; Rabouille and Gaillard, 1991; Wignall, 1991a; Paropkari et al., 1992). However, there is considerable evidence to suggest that a high organic carbon flux to the sediment caused by high surface water productivity may be the main mechanism for the formation of organic-rich sediments (Berger, 1979; Morris, 1987, Calvert, 1987; Bender et al., 1989). In this productivity model bottom-water anoxia may arise, but this is considered to be the result of a high oxygen demand unrelated to how much organic carbon is preserved. Pedersen and Calvert (1990) have highlighted the scant evidence for Woolnough's (1937) original contention and they challenge (p. 458) that, 'over a time scale of hundreds of years, there likely will be no significant difference in the amount of organic carbon preserved in oxic and anoxic sediments receiving more or less fresh organic matter.'

The preservation and productivity models are essentially incompatible because high productivity and

enhanced preservation conditions do not coincide (Tyson, 1987) despite the claims of many (e.g. Brongersma-Sanders, 1979; Legget, 1980). In the preservation model anoxic bottom waters are typically generated by stratification of the water column and the restriction of vertical advection (Chapter 7). As a result of the stratification, nutrients cannot be recycled into the surface waters once they have sunk through the density interface, with the result that surface-water productivity is typically low to moderate. It is important to stress that some productivity is still required in this model in order that there is a flux of decaying organic matter in the lower water column causing oxygen depletion. High-productivity conditions on the other hand, occur when there is an ample supply of nutrients (eutrophic conditions) supplied either by upwelling of deep waters or by a high influx of riverine nutrients (Diester-Haas, 1983). In contrast, then, high productivity is typically associated with much more dynamic and vigorous circulation.

Sedimentation rates in stratified basins are typically very low due to the occurrence of distinct depositional processes such as sedimentation from detached turbid layer suspensions (Section 2.2.2) whilst rates are generally much higher in high-productivity areas (Stein, 1986). Since the influential study of Muller and Suess (1979), many workers consider that high sedimentation rates may themselves be one of the most important factors favouring organic C accumulation (Ibach, 1982; Calvert, 1987; Rabouille and Gaillard, 1991). Thus, the preservation/productivity debate is even more polarized between a slow sedimentation rate/low-productivity model and a high sedimentation rate/high-productivity model (Table 6.1). Despite the obvious major differences in the predictions of these two models it is surprisingly difficult to eliminate either model when studying ancient black shales due primarily to our very poor ability to determine palaeoproductivity levels (Section 6.4) and sedimentation rate. Many studies assume that elevated organic carbon values are indicative of high productivity (e.g. Pratt and King, 1986; Herbert et al., 1986). This is the underlying assumption behind Bralower and Thierstein's (1984, 1987) sophisticated use of modern empirical

	Preservation	Productivity		
Water column	Stratified, lower water column overturned slowly	Well mixed		
Primary productivity	Low-moderate (1-100 g/cm <sup>2</sup> /yr)	High (200-600 g/cm²/yr)		
Sediment accumulation rates	Low (100-10 cm/1000 yrs for sediments of 60% porosity)	Usually high (1–10 m/1000 yrs for sediments of 60% porosity)		

**Table 6.1.** Depositional conditions implicit in the preservation and productivity models—rival models invoked in the formation of black shales

data to produce a predictive graph for measuring palaeo-productivity. But, in no case is it possible to eliminate the possible alternative that the elevated organic carbon values are the result of enhanced preservation under anoxic bottom waters.

The following sections summarize the pertinent evidence concerning the productivity/preservation debate and I hope to show that the available evidence, particularly from the geological record, indicates that the preservation model may be more generally applicable to black shale deposition.

# 6.2 OXIC VERSUS ANOXIC BREAKDOWN OF ORGANIC MATTER

It is implicit in many black shale studies that anoxia enhances both the amount of organic C preserved (Reimers and Suess, 1983; Bralower and Thierstein, 1984) and the quality or hydrogen-richness (Demaison and Moore, 1980). Therefore it is rather surprising that the empirical evidence to support this contention is rather equivocal. Foree and McCarty (1970) were amongst the first to demonstrate that organic matter oxidation rates by aerobic and sulphate-reducing bacteria were very similar; a conclusion supported by many subsequent studies (Henrichs and Reeburgh, 1987; Kristensen and Blackburn, 1987; Henrichs, 1992). Sulphate reduction rates are only appreciably reduced at low temperatures (Westrich and Berner, 1988) or at unusually high salinities associated with evaporite precipitation (Klinkhammer and Lambert, 1989). Neither condition is apposite to the deposition of most black shales-although see Kirkland and Evans (1981) and Section 7.4.2.

Canfield (1989a, 1992) has amassed a large data set of measured carbon oxidation rates (COR) and sediment accumulation rates (SAR) from numerous modern marine environments in conditions ranging from oxic to euxinic (Fig. 6.1). Essentially the two rates show a positive correlation (discussed further in the following section). In oxic settings under relatively slow sedimentation rates COR are significantly faster in the surface oxic zone than in the underlying sulphate reduction zone (Fig. 6.1); a phenomenon caused by the destruction of the most labile organic C in the surface sediment before it crosses the redox boundary. As SAR increase the oxic zone becomes progressively thinner causing the distinction between organic C oxidation rates in the oxic and sulphate reduction zones to become less until, at rates greater than 0.1 g/cm<sup>2</sup>/yr, values of COR are the same. Significantly, Canfield's data also show that in euxinic environments, where organic C is only oxidized by sulphate reduction, rates are indistinguishable from COR by oxic respiration (Fig. 6.1(b)). It is findings such as this which are at the heart of the productivity 'school's' argument that the preservation model is invalid, for there is little distinction in organic C preservation in oxic and anoxic settings (e.g. Pedersen and Calvert, 1990).

The productivity model considers that organic-rich sediments are formed by a high flux of organic C to the sea floor, irrespective of benthic oxygen levels. Calvert, the main advocate of this model, has documented several cases. For example, laminated strata accumulating in the oxygen minimum zone of the Gulf of California has similar TOC, HI, and OI values to bioturbated sediments forming above and below the zone (Calvert et al., 1992a). However, Calvert and his colleagues only studied sediments from the top 2-5 cm of gravity cores which, as van Cappellen and Canfield (1993) noted, have not undergone a complete sequence of diagenetic processing. Therefore, it is unsafe to conclude from this data alone that there is no diference in the burial efficiency of organic carbon in the two sediment types. Calvert (1987) similarly found no oxygen-related dependence to the amount of organic C



Fig. 6.1. Depth-integrated organic C oxidation rates plotted as a function of sedimentation rate for (a) oxic respiration and sulphate reduction beneath the zone of oxic respiration in aerobic sediments (b) sulphate reduction in sediments beneath a euxinic water column where no oxic degradation of organic matter occurs in the sediment (taken from Canfield, 1992). Note that the use of depth-integrated values 'smooths' the heterogeneous effect of bioturbation.

in the sediments of oxic and anoxic fiords. He has therefore concluded that, 'The hypothesis that hydrogen-rich organic matter [preferentially] accumulates under oxygen minima [the preservation model] is therefore falsified' (Calvert *et al.*, 1992a, p. 759). However, simply documenting the amount of organic C present in a sediment fails to fully test the hypothesis for the preservation model which predicts that *proportionally more* organic C survives in anoxic conditions. The actual amount of organic C present in the sediment is not implicitly predicted as this also depends on several other factors. Preservation is most directly measured by the burial efficiency (Henrichs and Reeburgh, 1987) where:

# burial efficiency = burial carbon flux/deposition flux $\times 100$ (% C preserved).

Canfield (1992) has calculated the burial efficiency for several euxinic, dysoxic, and oxic environments and plotted them as a function of SAR (Fig. 6.2). This shows that organic C accumulation is favoured by higher sedimentation rates, particularly in oxic environments, but, significantly, at lower sedimentation rates preservation is considerably greater in dysoxic to anoxic environments—the prediction of the preservation model. Figure 6.2 may also explain Calvert's findings, for his examples come from settings with high sediment accumulation rates where there is indeed little distinc-

tion in the burial efficiency between oxic and anoxic conditions. The results of Fig. 6.2 appear rather paradoxical when compared with those of Fig. 6.1 which fails to distinguish any oxygen-related differences in COR. However, Canfield (1992) suggests that at low sedimentation rates carbon preservation is low and only very small changes in the depth-integrated rates of carbon oxidation are required to significantly change carbon preservation. The subtle decrease in COR is too small to be resolved by Fig. 6.1. Just what causes this decrease is central to the preservation/productivity debate. Possibly, anaerobic microbes may only be able to utilize a limited range of organic substrates (Laanbroeck and Veldkamp, 1982). However, in an experimental study of the breakdown rates of specific monomers, Lee (1992) showed that, in general, there was little variation in rates between oxic and anoxic conditions, although a few compounds, such as formaldehydes, decomposed more slowly in anoxic waters. However, polymeric compounds, more typical of the organic matter encountered in natural environments, may degrade more slowly in anoxic conditions (Canfield, 1989a; Lee, 1992; Rudnick et al., in press) although this has yet to be proved.

The absence of bioturbation in anaerobic sediments is commonly held as one of the most likely causes of enhanced organic C preservation (Demaison and Moore, 1980; Yingst and Rhoads, 1980; Reimers and



Fig. 6.2. Burial efficiency (% carbon preserved) versus sedimentation rate for a) aerobic sediments and b) dysaeorobic and anaerobic sediments (taken from Canfield, 1992). Note that at low sedimentation rates burial efficiency is noticeably less in aerobic sediments.

Suess, 1983; Aller and Mackin, 1984; Pelet, 1987; Tyson, 1987; Aller and Aller, 1992; Henrichs, 1992; Lee, 1992). Bioturbation increases the residence time of organic C at the sediment surface (where the most intense oxidation occurs) by reworking and recycling the surface layers. Burrowers also aid the diffusion of oxidants into the sediment by their irrigating effectburrow walls are commonly the sites of the most intense bacterial activity (Demaison and Moore, 1980; Kristensen and Blackburn, 1987). More directly, the macrofauna and meiofauna may ingest organic material that is not prone to microbial attack. Bacterial organic matter in particular is resistant to bacterial degradation whilst nematodes and foraminiferans are able to ingest bacterial biomass (Jumars, 1989). Several authors have suggested that the process of irrigating the sediment flushes out the metabolic end-products of bacterial activity, such as H<sub>2</sub>S, which would otherwise reduce bacterial growth rates (Yingst and Rhoads, 1980; Henrichs, 1992). However, the recent results of Rudnick et al. (in press) suggest that bacterial metabolites are not inhibitory.

Whilst all these processes can be achieved by meiofaunal activity, macrofauna are generally the most important agents, particularly of irrigation. For example, solute transport rates of oxygen occur three times faster in sediment with an infaunal macrofauna than in sediment with a meiofaunal population alone (Aller and Aller, 1992). Therefore the burial efficiency of organic C in lower dysaerobic sediments (which have a meiofaunal but not a macrofaunal population) should be comparable with those in anaerobic sediments; a prediction supported by Canfield's (1992) data.

#### 6.3 THE INFLUENCE OF SEDIMENTATION RATE

The seminal study of Muller and Suess (1979) related the organic C content of sediment to two factors, primary productivity and sedimentation rate in a relationship given by:

% organic C = 0.003 
$$RS^{0.3}/p_s(1-\phi)$$

where S = sedimentation rate (cm/1000 yrs), R =primary production rate (g C/m<sup>2</sup>/yr),  $p_s = dry$  sediment density (g dry sediment/cm<sup>3</sup>),  $\phi = W/p_s W + (1 - W)p_w$ and W = % water of wet weight/100. No account is taken in this equation of the influence of oxygen variations as it is derived from Pleistocene oxic, hemipelagic settings. Muller and Suess' equation predicts that, for a tenfold increase in sedimentation rate, organic C values will double. Thus sedimentation rate was shown to be a potentially important control of organic C accumulation and in many subsequent studies it has been ranked as one of the principal controls (e.g. Arthur et al., 1984; Bender et al., 1989). This culminated in Ibach's (1982) proposal that the occurrence of source rocks could be predicted solely by locating areas within basins with high mudrock accumulation rates. As shown in the previous section, increased burial efficiency may indeed be achieved by higher SAR (Fig. 6.2) but it is rather naive to consider that it is the overriding control of organic C preservation.

Higher sedimentation rates are also associated with higher rates of sulphate reduction (Toth and Lerman, 1977; Berner, 1978) and organic C oxidation rates (Fig. 6.1). It is therefore not immediately apparent why organic C values should increase with sedimentation rate. Presumably the amount of organic flux to the sea floor increases in step with the increase in sedimentation rate, thereby fuelling more sulphate reduction, whilst the proportion of organic C mineralized becomes less due to its shorter residence time in the surface sediments. A similar line of reasoning is used to explain the positive S/C plots obtained from aerobic marine sediments (Section 4.3). A further cause may lie in the increase in the proportion of terrigenous organic C with sedimentation rate which would be less prone to oxidation than marine organic C-variations of organic matter type are not considered in the Muller and Suess equation.

The Muller and Suess equation and its ramifications have received substantial criticism, and it is clear that the importance of sedimentation rates to organic C preservation has been over-stated. The equation fails to account for the increasing turbidity associated with increasing fine-gained sedimentation rates which should reduce the primary productivity (Aller and Mackin, 1984). Also, at very high sedimentation rates any beneficial effects of enhanced preservation are counter-balanced by the dilution of the sediment organic C component by terrigenous clastic material (Demaison and Moore, 1980; Tyson, 1987). Maximum organic C values should occur at some optimum sedimentation rate. Jumars (1989) has also criticised Muller and Suess' approach as it reduces all benthic processes to one empirical function, sedimentation rate. As discussed above, rates of bioturbation are probably more apposite to discussions of organic C preservation.

Berger *et al.* (1989) have used the Muller and Suess equation to show that changes of sedimentation rate spanning a realistic range of mudrock sedimentation rates fail to alter organic C values by more than 40% whereas actual values of organic C vary by several orders of magnitude. Clearly other factors, not considered in the equation, are also important. This is further demonstrated by the occurrence of black shales in the geological record.

Black shales are typically highly condensed stratigraphic units confined to basin-centre locations but which pass into thicker shallower marine facies around the basin margin (e.g. Nixon, 1973; Broadhead et al., 1982; Wignall, 1991a). It is commonly not possible to calculate absolute sedimentation rates (Section 2.4 highlights the dangers of using varves) but it is apparent that most black shales are amongst the most slowly accumulated horizons seen in sedimentary basin fills. In a rare example, Mangini and Dominik (1979) were able to calculate the sedimentation rates of a Late Pleistocene sapropels as 7-8 mm/1000 yrs-a value that is typical of many organic-rich sediments. Maynard's (1980) sulphur isotope study of black shale pyrite further demonstrated the exceptionally low sedimentation rate of this facies. High sedimentation rates (e.g. 1 m/1000 yrs or greater, Table 6.1) are probably responsible for the accumulation of some organic-rich sediments, of which the several cases documented from recent fiords are probably the best examples (e.g. Calvert, 1987; Paetzel and Schrader, 1992).

In summary, there is clearly a dichotomy of mechanisms for black shale formation. Whilst slow sedimentation rates, anoxic bottom waters, and low productivity are probably responsible for many ancient black shales, evidence from recent environments indicates that conditions of high sedimentation rate and/or high productivity may also be responsible in some cases. Distinguishing between these two scenarios is of paramount importance in constructing black shale depositional models but, as shown in the next section, measuring palaeoproductivity is a difficult undertaking.

# 6.4 MEASUREMENT OF PALAEOPRODUCTIVITY

High surface water productivity is usually associated with a high flux of organic matter to the sea floor and therefore, it is commonly assumed, with organic C-rich sediments (e.g. Muller and Suess, 1979; Bralower and Thierstein, 1987; Sarnthein et al., 1988). Unfortunately it is unrealistic to expect such a direct correlation, as the burial efficiency of such a highly 'labile' nutrient as C is also controlled by variations of oxygen level and sedimentation rate. The first variable can be reasonably quantified (Chapters 2-4) but the second is very difficult to measure in any precise way. Concentrations of the other nutrients P and N are equally poor productivity measures as they undergo intense recycling in the water column and generally only an insignificant fraction of these elements is sedimented from the aquatic reservoir. Thus P concentrations in recent sediments are poorly correlated with surface water productivity (O'Brien and Veeh, 1983). In contrast Si is much more slowly reworked and over 90% of organic Si production is commonly preserved in sediment (Brumsack, 1989). Fluctuations in biogenic silica abundance are therefore commonly used as a proxy for primary organic C production (e.g. Murchey and Jones, 1992). Implicit in this approach is that changes in the abundance of siliceous plankton (for which Si is an important nutrient) closely parallel changes in the plankton as a whole. This is not necessarily the case (e.g. Qiu et al., 1993), and it is likely to be unreliable for quantitative estimates, but it may still be a qualitatively valid assumption because, in present-day oceans, siliceous diatoms are the dominant phytoplankton in areas of high nutrient abundance (Margalef, 1978).

Nonetheless, considerable care must be taken in interpreting ancient chert deposits for several factors may control their occurrence. High Si content can simply be the product of clastic-sediment-starved pelagic deposition such as that which occurred around the Late Jurassic Tethyan Ocean (Weissert, 1989). Furthermore, temperature rather than nutrient level may be a more fundamental control of siliceous plankton production, particularly diatoms (Berger *et al.*, 1989). Therefore it is not very surprising that Si-rich and organic C-rich sediments are not always closely associated in the geological record (e.g. Kuhnt *et al.*, 1986).

Rather than use Si, several authors have proposed the use of Ba concentrations, commonly expressed as the Ba/Al ratio, as a measure of palaeoproductivity measure (Schmitz, 1987; Jumars, 1989). The ocean chemistry of Ba is closely linked with nutrients such as Si, and it appears to be removed from solution as syngenetic barite produced in association with siliceous phytodetritus (Bishop, 1988). However, due to the time taken for barite formation in the water column, the association of high Ba concentrations and sites of high productivity is only seen in very deep water settings; there is little correlation in shallow water (von Breymann et al., 1992). Furthermore, any primary productivity signals may be lost as Ba is highly mobile during diagenesis, particularly within the sulphate reduction zone (Arthur and Dean, 1991; van Os et al., 1991; Shimmield, 1992).

The search for a palaeoproductivity index is clearly fraught with difficulties. No biomarkers for high or low productivity appear to be forthcoming (Brassell and Eglinton, 1983; ten Haven et al., 1992) whilst macropalaeontological criteria are controversial. Coveney et al. (1991) suggested that the abundance of well preserved fish in some Pennsylvanian black shales is evidence for high productivity and high sedimentation rates. However, the presence of fossil fish could just as easily reflect the exceptional preservation conditions of black shale deposition caused by the generally low benthic current velocities and the absence of scavengers in anoxic bottom waters (Jenkyns, 1985). In lowest dysoxic conditions, fish carcasses may remain undisturbed and articulated beneath a protective blanket of bacteria or fungi (e.g. Keupp, 1977). The presence of a diverse assemblage of marine reptiles and fish in the organic-rich shales of the Lower Oxford Clay (Middle Jurassic) suggested to Hudson and Martill (1991) a well developed food chain and therefore high productivity. It is difficult to test this conclusion as the marine vertebrates from aerobic facies are much more poorly known due to their lower preservational potential in such facies (Martill, 1985).

In summary, all fields of research (palaeontology and both inorganic and organic geochemistry) have thus far failed to provide a reliable means of assessing ancient productivity levels; as Berger *et al.* (1989, p. 27) noted, we are dealing entirely with guesswork.' One of the few hopeful avenues of research lies with carbon isotope studies.

# 6.4.1 The Lake Greifen model

By developing the work of McKenzie (1982, 1985), Hollander et al. (1992) have produced a model which, they claimed, can distinguish between productivity and preservation-generated organic-rich strata in the geological record. They take as their example a small Swiss lake, Lake Greifen for which records of water chemistry are available for the past 50 years and sedimentological data from cores stretch back to the late eighteenth century. Like many temperate-latitude lakes, Lake Greifen is seasonally stratified with a thermocline developed during the summer months and thorough mixing occurring during the stormy winter months. Initially, in the eighteenth century, primary productivity was not especially high and oxygen demand in the bottom waters was not sufficient to cause anoxia. However, over the last two centuries the increasing anthropogenic input of nutrients associated with agricultural and industrial activity has stimulated productivity and led to oxygen depletion. From 1932 the bottom waters became anoxic throughout the year and previously bioturbated sediments were replaced by laminated organic-rich limestones. Eutrophication culminated in 1974 with the development of anoxia to within six metres of the surface of the lake (Hollander et al., 1992).

A measure of the primary productivity is given by the inorganic and organic carbon isotope record from the lake sediments. Photosynthetic fixation of carbon produces particulate organic carbon (POC) enriched in 12C relative to the original  $CO_{2(aq)}$  whilst the formation of biogenic carbonate involves little or no isotope fractionation. Experiments with aquatic plants have shown that a decrease in the concentration of  $CO_{2(aq.)}$ , such as that associated with increasing productivity, causes a decrease in isotope fractionation (Hollander and McKenzie, 1991). Therefore a measure of the intensity of fractionation and thus the productivity can be had from the difference in the carbon isotope values of organic matter and biogenic calcite (lower values indicating higher productivity) which is given by the notation  $\Delta \delta^{13}C_{\text{calcite-organic matter}}$  ( $\Delta \delta^{13}C_{\text{cal-om}}$ ). Measurement of this value in the Lake Greifen sediments reveals two distinct stages during the development of eutrophication (Fig. 6.3-herein informally called a Hollander plot).

Samples from stage 1, which lasted until 1932, show a positive correlation of HI and  $\Delta \delta^{13}C_{cal-om}$ , whilst from 1932 to the present day HI continues to increase but there is a negative correlation. Hollander *et al.* (1992) explained these variations by changes in the proportion and amount of organic matter recycling in the water



Fig. 6.3. Hollander plot of the hydrogen index (HI) and  $\Delta \delta^{13}C_{cal-om}$  for sediments accumulated in Lake Greifen oven the last 200 years (from Hollander *et al.*, 1992), illustrating first a positive correlation up to 1932 (stage 1) followed by a negative correlation (stage 2).

column (Fig. 6.4). During stage 1 a large proportion of the organic matter is oxidized before reaching the lake floor thereby returning <sup>12</sup>C-rich CO<sub>2</sub> to solution whereby it is preferentially fixed during photosynthesis to produce very light organic matter. Hollander et al. (1992) thereby imply that values of  $\Delta \delta^{13}C_{cal-om}$  are not a direct measure of productivity as recycling also controls its value. Although the presence of bioturbated sediments suggests that permanent anoxia was not developed at this time, transient anoxia is said to have aided organic matter preservation and caused the increase of HI. During stage 2 productivity reached a level whereby CO<sub>2(aq.)</sub> concentrations became limiting to the plankton and the proportion of C derived from recycled, oxidized POC declined with a consequent decrease in isotope fractionation and values of  $\Delta \delta^{13}C_{cal-om}$ . The switch to permanent bottom-water anoxia at this time ensured the further increase of preservation quality and thus the continuing increase of HI.

The interpretation of the  $\Delta \delta^{13}C_{cal-om}/HI$  relationship by Hollander *et al.* (1992) appears sensible (it is also similar to Kuspert's (1982) interpretation of changes in  $\delta^{13}C_{om}$  values of some Toarcian black shales) but their further suggestion that the conditions of stage 1 are analogous to those of the preservation model and those of stage 2 to the productivity model is dubious. The only changing variable in the Lake Greifen model is productivity whereas, to truly test the preservation/ productivity models, changes in the intensity of stratification and circulation should also occur. In fact there is no evidence to suggest that there have been any changes in water column circulation of Lake Greifen over the last two centuries. The conditions of stage 1 are very unlike those proposed for black shales formed by enhanced preservation beneath anoxic bottom waters as oxic conditions appear to have been typical of stage 1. If anything, Lake Greifen provides substantial supportive evidence for the preservation model alone, because HI values in excess of 600 occur in bioturbated sediments indicating little oxygenrelated control of preservation. The high sedimentation rates in this lake-around 0.4 mm/yr-are probably the main reason for such high values because, as already discussed, at such high rates there is little distinction in the burial efficiency of organic C in oxic and anoxic settings (Fig. 6.2).

Nonetheless, Hollander plots probably provide one of the few indicators of if care is taken during analysis. The organic matter should be of uniform composition, as fluctuations in the proportion of terrigenous organic matter will change the values of  $\delta^{13}C_{om}$ . Rather than analyse the complete suite of organic molecules in the sediment, isotope ratios of porphyrins may prove to be a reliable measure of the  $\delta^{13}C$  values of aqueous algae (Hayes *et al.*, 1989). Carbonates must also be of surface water origin and not diagenetically altered (Hollander *et al.*, 1992).

Hollander plots of two European Jurassic black shales, the Kimmeridge Clay and the Schiste Cartones, show that the stage 2 relationship occurs in the former

#### THE LAKE GREIFEN MODEL



low nutrient/ CO2 ratio

 $CO_{2(aq)}$  unlimited, intense C isotope fractionation

# STAGE 2 (eutrophication)

high nutrient/ CO2 ratio

CO2(aq.) limited, less C isotope fractionation



Fig. 6.4. The two stages of the Lake Greifen model.

and the stage 1 pattern in the latter (Hollander *et al.*, 1991). This interesting observation may reflect relatively higher productivity in the Kimmeridge Clay seas but it does not necessarily suggest that the productivity model is apposite to this formation (cf. Section 8.2) because the influence of other important variables on Hollander plots is not known. For example, the degree of recycling of POC would decrease with a more intensely stratified (unmixed) water column whilst the associated decrease of nutrient availability would decrease productivity. Clearly, more empirical data from lakes would be welcome to investigate the influence of such effects.

#### 6.4.2 Nitrogen isotopes

The ratios of nitrogen isotopes in organic matter are controlled by a similar set of factors as carbon isotopes although their interpretation is even more complex than that for carbon isotopes as the oceanic nitrogen system is highly complex (Boyle, 1993). Nonetheless results from Holocene and Pleistocene sediments are encouraging. Nitrogen isotope fractionation principally occurs by the more efficient uptake of <sup>14</sup>N relative to <sup>15</sup>N by phytoplankton. Under conditions of nutrient overabundance, and therefore high productivity, the fractionation is most efficient leading to low (light) values of the <sup>15</sup>N/<sup>14</sup>N ratio. By using such ratios, preserved in organic matter, Calvert *et al.* (1992b) have shown that Pleistocene sapropels in the eastern Mediterranean accumulated during an interval of elevated productivity. In contrast, nitrogen isotope evidence from some Cretaceous black shales indicates their accumulation during low-productivity intervals (Arthur and Dean, 1991).

Nitrogen isotope ratios are affected by a range of interdependent oceanographic and biological factors. For example, the influence of nitrogen-fixing cyanobacteria in low-productivity settings can greatly alter nitrogen ratios (Rau *et al.*, 1987). Like many supposed palaeoproductivity indices, unravelling the various controlling factors in the geological record may prove insurmountable.

# NOTE ADDED IN PROOF

The preceding chapter has highlighted a fundamental debate in black shale studies. The recently reported modelling of the oceanic phosphorus cycle by van Cappellen (1993) may provide a solution to this current dichotomy of views-black shale depositional environments may in fact be characterized by both high productivity and the sluggish circulation associated with a stratified water column. In the modern oceans phosphorous is an important and limiting nutrient of primary productivity. However, in oxic conditions, it is rapidly scavenged from the water column by iron oxyhydroxides which have a great affinity for this element (Berner, 1973). In anoxic waters this effect does not occur, iron forms sulphide species as discussed in Chapter 4 whilst phosphorus forms soluble species (Berner, 1977). Therefore anoxic bottom waters regenerate phosphorus and release it to the upper water column thereby facilitating higher productivity. Organic phosphorus compounds are broken down but the phosphorus is not scavenged by iron oxyhydroxides. Modelling shows that this effect is of such significance that it overrides any counteracting effect that decreased circulation (associated with the establishment of a stratified water column) may have upon nutrient recirculation (van Cappellen, 1993). The importance of redox chemistry to the oceanic phosphorus cycle has been previously recognized by Malkowski et al. (1979) in their model for the Permo-Triassic mass

extinction. They proposed that during this interval there was a transition from 'overfed' Permian oceans, in which anoxic deep waters efficiently regenerated phosphorus, to 'hungry' Triassic oceans where an entirely oxic water column was an efficient phosphorus sink.

It could be considered that, whith an ample supply of phosphorus in anoxic settings, nitrogen would become the limiting nutrient. However, van Cappellen (1993) noted that, when nitrate contents become low, N<sub>2</sub>-fixing autotrophs may become important, thereby utilizing an essentially limitless nutrient. Apparent support for van Cappellen's model comes from Ingall and Jahnke's (1993) compilation of organic C/organic P ratios for mudrocks. This shows that black shales have C/P ratios an order of magnitude higher than those of normal marine mudrocks. Clearly implicit is the greatly decreased burial flux of phosphorus in black shale sediments. Presumably, this effect more than counteracts any effect a decline in sedimentation rate may have on the phosphorus content of the sediments. As discussed in Section 6.3, black shales typically form at very low sedimentation rates; the concentration of biogenic calcium phosphate material (such as fish bones and conodonts) should increase with declining sedimentation rates. A further ramification of the model is that a significant proportion of the lower water column is required to be anoxic for the recycling of phosphorus. In other words black shales presumably form in euxinic environments rather than in conditions where the redox boundary is located around the sediment surface.

Van Cappellen's model neatly unites the two polarized views of black shale formation. The development of anoxia in the lower water column creates higher productivity which in turn leads to higher organic carbon flux to the sediment and intensification of oxygen removal. Therefore, once anoxia is established a positive-feedback mechanism operates or, as van Cappellen (1993, p. A-365) noted, 'the development of anoxia may be autocatalytic'. Whether anoxia actually enhances the preservation of organic carbon remains a separate, contentious, issue. A further question that still remains to be addressed is what conditions lead to the development of bottom water anoxia in the first place? The nature of this triggering mechanism is addressed in the following chapters.

# Modern analogues for black shale formation

Undoubtedly many of the uncertainties concerning black shale formation stem from a lack of directly comparable modern day analogues. Most black shales in the geological record accumulated in the deeper parts of epicontinental seas which, by definition, had only poor to moderate connection with the world's oceans (Hallam, 1981; Klemme and Ulmishek, 1991). There are rather few epicontinental seas at present, and the more common shelf seas are not sites of enriched organic C accumulation. None the less, organic-rich sediments are currently found in several distinct settings and our understanding of their genesis can provide diagnostic criteria for the recognition of comparable sites in the past.

# 7.1 THE BLACK SEA-A STRATIFIED, SILLED BASIN

The modern-day Black Sea is the largest anoxic basin in the world and its has long been identified as a good analogue for ancient black shales (e.g. Pompeckj, 1900; Tyson *et al.*, 1979). The basin is almost landlocked as connection with the Mediterranean is via the Straits of Bosporus; a highly tenuous link less than 30 m deep in places.

The Black Sea receives large volumes of fresh water from rivers draining its northern hinterland and is also supplied with marine water from the Mediterranean. The relative proportions are such that the Black Sea has a positive water balance with 340 km<sup>3</sup> of brackish water leaving the basin each year and only half this amount (176 km<sup>3</sup>/yr) of marine water entering as an underflow through the Bosporus (Stanley and Blanpied, 1980; Fig. 7.1). Due to the density contrasts between these waters of differing salinity a halocline is developed at a depth of around 200 m within the water column. This severely restricts the vertical advection of oxygen-rich surface waters to the depths. Lateral advection is also highly restricted due to the small amount of water entering the basin relative to the basin's volume. Thus, circulation is



Fig. 7.1. The modern-day Black Sea—a model for ancient black shale environments? A vertical scale is given but no horizontal scale is implied.
extremely sluggish beneath the halocline and around a thousand years is required for complete mixing of the lower water column (Brumsack, 1989). As a consequence of the poor circulation and a moderate oxygen demand from decaying and descending organic matter, the lower water column beneath the halocline (the monimolimnion) is anoxic and contains free hydrogen sulphide—the definitive euxinic condition.

The sediments accumulating in the deeper parts of the Black Sea consist of fine siliciclastic turbidites (Lyons and Berner, 1992) interbedded with organic-rich, microlaminated limestones (Bukry et al., 1970). The carbonate-rich laminae are composed almost exclusively of the coccolithophore Emiliana huxleyi which is thought to bloom during intervals when nutrients, normally trapped beneath the halocline, are mixed into the euphotic zone (Bukry et al., 1970). The marine organic matter of the sediments may be derived from photosynthetic anaerobic bacteria (the Chlorobiaceae) living in the uppermost monimolimnion. Mass mortality of the bacteria generally occurs every winter when they are mixed into the oxygenated upper water column thereby producing the dark laminae seen in the sediments (Degens and Stoffers, 1980). Alternatively, seasonal fluxes of diatoms in the spring months and coccolith blooms in the summer may produce the lamination (Dickman and Artuz, 1978; Sinninghe Damste et al., 1993). Despite the conflicting models for laminae formation, both interpretations imply that the dark-light lamination couplets represent annual varves which can therefore provide a detailed year-by-year chronostratigraphic record. However, doubt was cast on the varve interpretation (e.g. Degens and Stoffers, 1980) by the discrepancy between ages from varve counting and the considerably older ages from carbon-14 radiometric dating (Dickman and Artuz, 1978). Although sediments may incorporate 'old' organic C during their accumulation, radiocarbon ages generally provide a more reliable estimate of the age of Holocene sediments. The so-called varve couplets appear to represent an average of three years' worth of deposition (Calvert et al., 1991; Lyons and Berner, 1992). Pelagic deposition is clearly a rather episodic process in the deeper Black Sea as further demonstrated by Lyons and Berner (1992) who document the sedimentation of organic 'fluff' layers-the product of phytoplankton productivity blooms-every 20 years or so.

The most organic-rich sediments of the Black Sea are encountered in the topographic lows on the basin floor and 'there is no correlation between phytoplankton production [which is highest adjacent to the sites of riverine input of nutrients] and organic matter in sediments' (Shimkus and Trimonis, 1974). The correlation of organic richness with hollows has been attributed to the 'centripetal effect' (Huc, 1988) whereby low-density organic particles and the finest-grained sediment are focused into such hydrodynamically quiescent regions by the sluggish internal currents of the Black Sea which tend to circulate around hollows. The resultant pattern of sedimentation resembles a 'bull'seye' with the most organic-rich strata at the centre of the eye.

Sedimentation within the Black Sea has varied considerably during the Holocene reflecting the changing position of relative sea-level and climatic variations. Therefore, although the finely laminated coccolith limestones accumulating at present have some similarities to ancient black shales (e.g. Tyson *et al.*, 1979), the sapropel that accumulated in the deeper parts of the Black Sea during the mid-Holocene is a far more suitable analogue (Fig. 7.2). Unfortunately we have little idea of water column conditions during its formation and there is thus considerable controversy as to the conditions in which sapropel formed and to the validity of the Black Sea analogue as a whole (Calvert *et al.*, 1991).

Holocene sediments of the deeper Black Sea are readily divisible into three units (Fig. 7.2); Unit 1 the coccolith limestone currently accumulating, Unit 2 an organic-rich sapropel, and Unit 3 a claystone. The lower part of Unit 3 contains freshwater dinocysts whilst in its upper part a marine influence becomes progressively more noticeable. Thus Unit 2 accumulated during a transition between lacustrine conditions and the modern-day marine, euxinic basin. The sapropels of Unit 2 initially began to accumulate in the deeper parts of the Black Sea around 6600 years ago and they rapidly expanded their extent so that by 6000 years ago they covered both the floor and the lower slopes of the basin (Glenn and Arthur, 1985). The transition from Unit 2 to 1 is diachronous with sapropels gradually reducing their areal extent until they are last recorded in the basin centre 1600 years ago (Calvert, 1990).

Organic C values and composition vary through Unit 2 with the most organic-rich lithology occurring at the base. On the basis of carbon isotope values, Calvert and Fontugne (1987) argued that marine organic matter dominated all Unit 2 deposition. However, their data show a spectrum of  $\delta^{13}$ C values which indicate a general up-section increase in the proportion of MOM but with a significant amount of terrigenous organic matter (TOM) in the basal beds, as suggested by many previous authors (e.g. Shimkus and Trimonis, 1974; Degens and Stoffers, 1980; Glenn and Arthur, 1985).

Two conflicting models are available for the inter-



Fig. 7.2. Holocene stratigraphy of the deeper parts of the Black Sea. Units 1-3 are those of Degens and Ross (1974), used in the majority of subsequent studies.

pretation of conditions during the deposition of Unit 2; they are described below.

#### 7.1.1 The Deuser model

The influx of marine waters into the Black Sea created a marine 'puddle' in the deeper parts of the basin which gradually expanded upwards. The lower water column is considered to have been effectively isolated from the surface, as minimal mixing occurred across the halocline. with the result that euxinic conditions were established (Fig. 7.3). This facilitated the enhanced preservation of organic C in deep-water sediments (Deuser, 1974). Changes in surface water productivity are not considered important in the Deuser model, although the progressive restriction of the size of the mixed upper water column, the mixolimnion, may have gradually restricted nutrient availability and thus led to a decline in productivity. The up-section decline in the TOC content of Unit 2 may therefore reflect decreasing productivity, although it may also have been caused by a decrease in the influx of TOM to the sediments.

The halocline probably reached its present position around 1600 years ago whereupon turbulent mixing across this boundary produced conditions favourable for coccolith blooms. The lower TOC values of Unit 1 compared with Unit 2 are probably due to the dilution effect of coccolith carbonate because, on a carbonatefree basis, the sediments of Units 1 and 2 have similar organic C values.

#### 7.1.2 The Strakhov model

The Deuser version of events invokes organic C accumulation as a result of enhanced preservation beneath an anoxic water column. In total contrast Strakhov (1971) and his recent champions (Calvert *et al.*, 1987; Calvert and Fontugne, 1987; Calvert, 1990) propose that Unit 2 accumulated as a consequence of elevated productivity. During the initial stages of the marine incursion into the basin, nutrients in the lowest part of the water column are envisaged to have remained isolated from the euphotic zone and so remain 'stored'. Ultimately the upward displacement of these waters by a rising monimolimnion releases the nutrients to the mixolimnion and triggers a highproductivity episode (Fig. 7:3). Thus the elevated organic C values of Unit 2 record a high flux of organic



Fig. 7.3. Competing models for the formation of Unit 2 sapropels in the Black Sea.

matter to the sediment at a time when the water column was fully oxygenated.

The Strakhov model as it stands fails to account for the details of Unit 2 stratigraphy such as the initial and final restriction of deposition to the deepest part of the basin. Therefore account must be taken of Huc's (1988) centripetal effect, with weak bottom currents concentrating organic matter into local hollows.

Using evidence from I/Br ratios, Calvert (1990) has claimed that the entire water column was oxygenated during Unit 2 deposition, thereby supporting the Strakhov model. In normal marine conditions both I and Br are incorporated into organic C. But, in anoxic settings, I/Br ratios are typically lowered because reactive iodate ions are reduced to unreactive iodide whilst Br speciation is unaffected by such redox changes (Wong and Brewer, 1977). In Black Sea sediments I/Br ratios from Unit 1 are consistently around unity, whilst a much greater variability is seen in Unit 2 both within sections and between cores, although ratios commonly exceed unity (Calvert, 1990). Thus Calvert (1990, p. 344) concluded, after 'allowing for some diagenetic loss of iodine with burial ... that the basin was oxygenated when the [sapropel] horizon formed."

In fact the wide range of ratios in Calvert's data could, on face value, be taken to indicate a plethora of redox states within the basin during Unit 2 deposition. However, the lack of correlation of any of the trends between cores suggests that a much more localized phenomenon than basinal conditions is controlling the I/Br ratio. I is highly mobile during diagenesis, being displaced from its organic matter sites by thiosulphate ions (François, 1987). Thus, I/Br ratios might be expected to decrease with burial in anoxic sediments although the lack of consistent trends in Unit 2 suggests that several factors may influence I chemistry. For instance, the up-section change of organic C composition in Unit 2 may also be important. Therefore there are considerable uncertainties in interpreting I/Br trends and it is not surprising that few studies have attempted to derive palaeo-oxygen values from such data.

Calvert (1990) also noted that some horizons within Unit 2 have elevated Mn concentrations (although again there is considerable variation between cores) which he attributes to  $MnO_2$  precipitation in a fully oxygenated water column. Alternatively, I would suggest that such local horizons could represent Mn-rich microturbidites that were derived from oxygenated slope settings but were deposited on the anoxic basin floor.

In summary, Calvert's (1990) geochemical evidence supports neither the Strakhov nor the Deuser model and it offers no truly diagnostic criteria to test either. The most significant feature of Calvert's data is the great variability of Unit 2 geochemistry which could indicate that the water column varied from intensely anoxic to fully oxygenated, or alternatively that other phenomena may be important. The recent study of biomarkers of the photosynthetic green sulphur bacteria (the Chlorobiaceae) has shown that they were sometimes present during deposition of the lower but not the upper part of Unit 2 (Sinninghe Damste *et al.*, 1993). This curiously suggests rather rapid changes in the nature of the Black Sea water column during the mid-Holocene.

Convincing evidence for the support of the Deuser model comes from the nature of the Unit 2 sediments. These are finely laminated and contain no *in situ* benthic fossils—strong evidence for the occurrence of persistent benthic anoxia (cf. Section 3.7). In noting this point, Pedersen and Calvert (1991, p. 501) have modified Calvert's (1990) original assertions somewhat and they considered that, 'the pore waters [became] anoxic to the sediment surface, and perhaps to the bottom waters.' It is difficult to see how MnO<sub>2</sub> could precipitate in these conditions as they suggested, and why such a thin veneer of bottom water anoxia was not frequently disrupted to produce oxygenation events which would be recorded as burrowed horizons within Unit 2.

The Deuser version of the Black Sea has been widely used as an analogue in the interpretation of many ancient black shales, particularly those frequently encountered in epicontinental seas. Clearly it is not an ideal analogue for it is substantially deeper than many epicontinental basins, probably by an order of magnitude, and a good deal more brackish. Nonetheless the Black Sea still provides several diagnostic criteria for the recognition of black shales formed in silled basin settings:

(1) The most organic-rich sediments preferentially accumulate in topographic lows due to the focusing of low density organic particles in such areas by weak currents (Huc, 1988). This gives rise to a 'bull's-eye' stratigraphic distribution (e.g. Fig. 5.3). Thus, by implication, there is no direct relationship between sites of high productivity in the surface waters and sites of black shale deposition. This is the essence of the preservation model discussed in Chapter 6. It is important to note that 'Great depth alone will not insure that a basin will become stagnant, as has often been implicitly assumed in the geologic literature' (Byers, 1977, p. 7) as the depth of the sill and its restriction of lateral advection of water masses is an unknown depth constraint.

(2) There is no correlation between organic matter

composition and the abundance of organic C for the preservation of organic C is attributed solely to enhanced burial efficiency in anoxic conditions. As burial efficiency is only appreciably enhanced under slow sedimentation rates (Canfield, 1989; Chapter 6) this criterion clearly implies that low sedimentation rates are a further diagnostic criterion for Black Seastyle black shale deposition (e.g. Glenn and Arthur, 1985; Brumsack, 1989). However, it is extremely difficult to determine absolute sedimentation rates in the geological record and such a criterion is unlikely to be widely applicable. Calculating average rates for successions that include black shale horizons is commonly possible (for example, the assumption that Jurassic ammonite zones lasted for one million years (Weedon, 1986) is commonly used as a starting point for assessing sedimentation rates). This has little bearing on black shale deposition because sedimentation rates can vary considerably within short sections as seen in the Black Sea during the accumulation of less than a metre of sediment in the Holocene (Calvert et al., 1987).

(3) Silled basin black shales can be closely interbedded with normally oxygenated facies (e.g. Fig. 7.2). The changes in Holocene Black Sea sedimentation have been driven by a glacioeustatic sea-level rise but eustasy need not necessarily be invoked for all facies changes in silled basins. For example, if the climate around the Black Sea were to become more arid, the increased evaporation of surface water could generate warm, saline waters which would sink and oxygenate the basin floor. This scenario occurs in the Mediterranean, another large silled basin, where the rapid rates of vertical advection ensures oxic deposition throughout the basin (Demaison and Moore, 1980). The close correlation of humidity with black shales and aridity with normal aerobic facies in this Black Sea/Mediterranean comparison has led many authors to propose that ancient successions of alternating black shales and mudstones are a product of humidity/aridity cycles (e.g. Seibold, 1970; Rossignol-Strick et al., 1982; Weedon, 1986; Cecil and Edgar, 1991).

Most ancient epicontinental sea black shales probably accumulated in much shallower basins with a considerably higher width/depth ratio. Consequently, in addition to the 10 000-year scale environmental variability driven by eustatic/climatic changes, these shallower basins were probably subject to much higher frequency storm perturbations (e.g. Wignall, 1989). As already noted (Chapter 3), the palaeoecology of many black shales records frequent short-term oxygenation events (Wignall and Myers, 1988; Sageman, 1989; Oschmann, 1991).

However, temporal instability is unlikely to be

uniquely diagnostic of silled basin black shales, for highproductivity systems are also strongly controlled by climatic variations on a variety of scales (Section 7.4.). Therefore the 'bull's-eye' stratigraphic occurrence is probably the most useful for the detection of silled basin black shales.

#### 7.2 TEMPERATE SHELF SEAS

Most modern shallow marine deposition occurs in shelf seas rather than epicontinental seas—the favoured location for ancient black shale deposition. However, Tyson and Pearson (1991) have suggested that the oceanographic conditions of shelves can be used in the modelling of black shale deposition.

Temperate shelf seas are subject to seasonal temperature stratification that may coincide with temporary oxygen deficency in the bottom waters. In winter months the water column is thoroughly mixed by the vigorous wind-driven turbulence associated with winter storms. Productivity is low at this time as the windmixed layer circulates phytoplankton beneath the euphotic zone where they die. With the onset of spring, the decrease in storminess causes the turbulent mixing to become progressively restricted to the upper water column. The development of a thermocline further restricts oxygen supply to the bottom water. Once the wind-mixed layer lies entirely within the euphotic zone, phytoplankton (typically diatoms) are able to thrive and they rapidly consume the nutrients. By the summer months the bottom waters commonly become oxygen depleted due to oxygen demand of the decaying spring phytoplankton bloom and the restricted circulation. The return of stormy conditions in autumn destroys the stratification and thoroughly mixes the water column.

Tyson and Pearson (1991) note that the extent of oxygen depletion is dependent upon several factors: the organic loading, the intensity of the pycnocline, the initial bottom-water oxygen content, the duration of the stratified period, and the volume of sub-pycnocline bottom water. They consider that, in the geological past, conditions in many epicontinental seas were suitable for the development of seasonally anoxic conditions comparable to but somewhat more intense than the seasonal oxygen deficiency seen in modern shelf seas. The oxygenated winter months may only have lasted a few months and thus there was insufficient time for benthic colonization and bioturbation. Seasonally stratified seas are not efficient nutrient traps due to the thorough winter mixing, and productivity may be quite high. This avoids a negative feedback mechanism of permanently stratified water column models in which nutrients are permanently lost beneath the pycnocline thus reducing productivity and oxygen demand in the lower water column.

Tyson and Pearson's seasonal model offers several predictive criteria for interpreting black shale environments. Thermoclines tend to be developed between 10 and 40 m water depth and therefore black shales must form at greater depths. Haloclines can develop at both shallower and deeper depths but they are of only local importance in modern shelf seas. The strong climatic control over all aspects of the model may cause black shale formation to be closely tied to Milankovitch-style climatic variables although this is not necessarily a uniquely diagnostic feature.

Tyson and Pearson (1991, p. 12) also considered that black shales will form in topographic lows where "focusing" of fine sediment and suspended organic matter' will lead to intense oxygen deficiency. This is an eminently sensible prediction but it merely reiterates one of the main characteristics of the silled basin model (Section 7.1). This apparent overlap in the predictions stems from Tyson and Pearson's inclusion of two very distinct shelf settings in their model-topographic lows, which are essentially silled basins by another name, and truly open shelf settings. Within the former category are various anoxic deep water fjords and the deep basins of the Baltic' (Tyson and Pearson, 1991, p. 12) whose situation is comparable to that of the Black Sea. In open shelf settings oxygen deficiency initially develops in shallow-water settings where the volume of sub-thermocline water is small and thus becomes more rapidly depleted of its oxygen than deeper areas (Armstrong, 1979; Rosenberg and Loo, 1988; Stachowitsch, 1991). Thus open shelf settings subject to seasonal oxygen deficiency should show the following facies distributions on a shallow to deep water transect:

(1) Shallow, aerobic facies formed above the pycnocline.

(2) Anaerobic/lower poikiloaerobic facies formed beneath a thin sub-thermocline layer at intermediate water depths.

(3) A deep water upper poikiloaerobic facies formed under conditions of less intense summer oxygen deficiency due to the immuring effect of a greater volume of bottom water beneath the pycnocline.

The prediction that the best black shales should form at intermediate water depths within a basin is distinct from the predictions of permanently stratified, silled basins and highlights why open shelf settings should be considered separately from silled basins/topographic lows.

The seasonal model has several attractive aspects. In

particular it may account for the interpretations of several workers who have suggested that many ancient black shales formed at intermediate water depths (e.g. O'Brien, 1990; Banerjee and Kidwell, 1991; Pasley et al., 1991; cf. Chapter 9). However, the model is probably inapposite for black shale formation for several reasons. None of the modern open shelf settings are currently forming black shale-like sediments. For example, intense dysoxic episodes have been recorded in the shelf seas of the northern Gulf of Mexico but the sediments consist of a heterolithic selection of bioturbated sands, silts, and muds (Harper et al., 1991). This is rather surprising as the high anthropogenic input of nutrients into the world's seas at present is probably greater than anything seen in the geological past. If modern eutrophic open shelves are incapable of forming black shales today then they are highly unlikely to have done so in the past.

A further argument against the seasonal model concerns the unlikelihood of preserving the fine, unburrowed laminae characteristic of many black shales in depositional environments subject to seasonal (winter) oxygenated intervals. Tyson and Pearson (1991, p. 17) argued that recolonization of the sediment would not occur in winter because of the, 'scale of the defaunated areas, and/or the highly reducing state of the sediment surface.' This seems unlikely given the ability of modern invertebrates to rapidly recolonize areas (once anoxia has abated) in a matter of weeks or months (cf. Section 3.2). It should also be noted that in many modern settings invertebrates are able to survive many months of anoxia if hydrogen sulphide is not present (Tunnicliffe, 1981).

The seasonal model is also not supported by geochemical evidence. The commonly observed authigenic U enrichment of many black shales would not occur if bottom waters were to become regularly oxygenated for even a few hours as the soluble uranyl ion forms rapidly in the presence of oxygen. allowing U loss into solution (Anderson *et al.*, 1989a; Section 4.5.5).

#### 7.3 OXYGEN MINIMA AND UPWELLING ZONES

Modern oceans are generally well oxygenated, particularly in their lower layers where Antarctic bottom waters provide oxygen to most areas of the world's ocean floor. As a consequence the oceans have little value as analogues for black shale studies. However, intermediate levels within the water column (typically between 500 m and 2000 m depth) are characterized

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by relatively low oxygen values (Southam et al., 1982). This oxygen minimum zone (OMZ) is caused by the oxygen demand of decaying organic matter as it descends through the water column. The depth to the top of the OMZ is controlled by the rate of downward advection of oxygen-rich surface waters—a process which varies little throughout the oceans. In contrast the lower boundary is controlled by the rate of upward advection of cold, oxygen-rich bottom waters which can vary significantly (e.g. Ingle, 1981). The Coriolis force deflects northward-flowing Antarctic bottom waters to the western side of the oceans causing the OMZ to be enhanced in eastern seas, as exemplified in the eastern south Atlantic (Demaison and Moore, 1980).

In principle, black shales could form where the OMZ intersects the continental slope, although this is not observed at present as the OMZ is rarely sufficiently intense for dysoxic conditions to occur. However, in past, non-glacial times, when deep ocean waters may have been warm and oxygen-poor (Brass *et al.*, 1982), the OMZ could have been both thicker and more oxygen deficient.

The relevance of the OMZ to black shale studies becomes more important in regions where upwelling of deep, nutrient-rich waters to the surface causes elevated productivity and therefore greater oxygen demand in intermediate waters. No less than ten distinct mechanisms are known to cause upwelling (Hay and Brock, 1992) but several, such as equatorial divergence, are only encountered in the open ocean. They are not associated with the accumulation of organic-rich sediments (Parrish, 1982). Coastal upwelling is the most important variety of upwelling and the majority of the world's dysaerobic sediments form in these areas. It occurs on north-south coasts between 10° and 40° latitude on the east side of oceans where strong, coastparallel winds deflect surface waters offshore causing deeper, nutrient-rich waters to upwell in their place. Oxygen deficiency beneath upwelling zones can reach suboxic levels and it can also be extensive; the OMZ off south-west Africa covers an area of 50 by 340 km (Calvert and Price, 1971).

Anoxic to dysoxic deposition occurs at the intersection of the intensified OMZ with the upper slope and outer shelf of continental margins and may occur in water depths as shallow as 50 m (Fig. 7.4). A range of bottom-current velocities and substrate types are encountered in upwelling zones (Savrda *et al.*, 1984). Organic particles only accumulate in low current velocity settings in association with other fine-grained



Fig. 7.4. Simplified dynamics of a coastal upwelling system.

material (Suess *et al.*, 1987). As noted in Chapter 6, siliceous plankton tends to be abundant in nutrient-rich conditions, with diatoms dominant at high latitudes and radiolarians at low latitudes (Pisciotto and Garrison, 1981), leading to silica-rich sediments. Deposition around the upper and lower boundaries of the OMZ is marked by concentrations of phosphate-rich sediment which, if subject to prolonged winnowing by bottom currents, may be concentrated into almost pure phosphorites (Demaison and Moore, 1980; Loughman, 1984).

The organic-rich accumulation in upwelling zones is due to elevated productivity levels in a regime of vigorous circulation whilst the oxygen deficiency is a consequence of the high organic loading. Nonetheless the presence of oxygen deficiency also aids the preservation of organic C because organic-rich sediments are only forming in upwelling zones with a well developed OMZ. For example, the very high productivity around the shores of Antarctica is not reflected by high organic C values of the sediment in this region due to the exceptional oxygen-richness of the cold waters (Demaison and Moore, 1980).

A variant on the upwelling zone theme occurs in the silled basins of the California Borderland. The basins with sills within the OMZ are subject to anaerobic or dysaerobic deposition (Blake, 1981; Donegan and Schrader, 1981). The Santa Barbara Basin is amongst the best studied of the California Borderland basins and it shows an interesting degree of temporal variability (Reimers *et al.*, 1990). During the spring months intense upwelling spills deep, cold, oxygen-rich water over the sill and temporarily elevates bottom-water oxygen levels. In the autumn months upwelling is less intense and low dysoxic conditions are developed favouring the growth of bacterial mats.

Turbidites commonly transport both sediment and oxygen-rich waters into upwelling zones causing temporary oxygenation events that may trigger brief benthic colonization events (Sholkovitz and Soutar, 1975). Some benthic fauna may even be transported alive into the OMZ by turbidites-the 'doomed pioneers' of Follmi and Grimm (1990). On a larger scale, entire upwelling zones may fail in some years if longshore winds cease. Such celebrated 'El Niño' events cause a decline in productivity and there is therefore less oxygen demand within the OMZ (Quinn et al., 1987). However, generally, OMZs associated with upwelling are stable on a decade-to-decade scale (Wignall, 1990b) whilst oxygenation events tend to be on a once-in-a-hundred-years scale (Soutar et al., 1981).

Several diagnostic criteria are available for the

recognition of ancient black shales formed beneath upwelling zones.

(1) Black shales formed by coastal upwelling should be palaeogeographically restricted to the low latitude, western margins of continents.

(2) Oxygen-deficient sedimentation beneath upwelling zones tends to occur in long, narrow zones parallel to the coastline. Therefore a time-slice through black shales formed in these settings should reflect this ribbon-like geometry. This contrasts with the more sheet-like geometry of black shales from silled basins.

(3) Upwelling is a result of a highly dynamic circulation episodes. Therefore intervals of black shale formation should coincide with evidence for increased current activity within the depositional environment, although the actual depositional site of the black shales occurs in low current velocity settings.

(4) There should be an intimate association of black shale facies with cherts (radiolarites, diatomites) and phosphorites. However, the ideal arrangement of phosphatic facies bounding organic-rich strata is rarely observed; Loughman (1984) documented one of the few good examples from the Jurassic Aramachay Formation of Peru. The Permian Phosphoria Formation of the United States Western Interior is a good contender for a major stratigraphic unit formed during upwelling (it accumulated in a westerly facing continental margin basin at low latitude) but there is little ordered arrangement of facies types in this chertdominated formation (Maughan, 1984).

Clearly the most conclusive evidence for upwelling is derived from regional scale stratigraphic data whilst purely outcrop scale evidence is of little diagnostic value. Palaeoecological analysis can record the temporal instability caused by El Niño events for example, but fluctuating conditions are also a feature of black shales from silled basins (Section 7.1). Similarly the search for a biomarker to characterize high-productivity settings has thus far failed (ten Haven *et al.*, 1992). Biomarkers for gliding bacteria have been proposed although none are known (Repeta *et al.*, 1992), and such bacteria are in fact diagnostic of suboxic conditions not high productivity, upwelling settings *per se*.

Upwelling is considered by some authors to be responsible for a significant proportion of black shales; Parrish (1982, 1987) suggests between a third and a half. A good deal of this estimate is based upon her assumption that open ocean phenomena such as equatorial divergence operated in the epicontinental seas of the past, the principal site of much black shale deposition. In fact very few black shales formed in continental margin settings (the Phosphoria and Monterey Formations of the western United States are notable exceptions), the expected location based upon comparison with modern-day upwelling zones (North, 1979).

#### 7.4 LAKES AND LAGOONS

#### 7.4.1 Lakes

As in the marine realm, the oxygen levels in the bottom waters of lakes are controlled by the oxygen demand (a function of the surface water productivity) and the rate of supply of dissolved oxygen. Nearly all temperate and high-latitude lakes are fully oxygenated throughout the water column due, amongst other factors, to the development of cold, oxygen-rich suface waters in winter which sink to the bottom causing overturn of the water column. Only those lakes subject to a high anthropogenic input of nutrients are currently suffering oxygen deficiency (e.g. Lake Greifen, Section 6.4.1). However, at low latitudes, where there is little seasonal variability, thermal stratification is seen all year round and anoxic bottom waters are commonly developed, particularly when productivity is high (Demaison and Moore, 1980).

Anoxic lakes appear to provide superlative conditions for the preservation of organic matter as nearly all Type I kerogens are of lacustrine origin (Kelts, 1988). Several factors appear to combine to aid preservation. The absence of sulphate reducing bacteria in freshwater lakes ensures that, once the dissolved oxygen has been consumed, only inefficient methanogenic processes are available to continue the breakdown of organic matter (Kelts, 1988). Conversely, sulphate reduction is considerably retarded in hypersaline lakes (Bauld, 1981; Klinkhammer and Lambert, 1989). Many of the best source rocks appear to have formed in alkaline lakes (e.g. Bradley, 1973; Boyer, 1982; Parnell, 1988). However, in these conditions sulphate-reducing bacteria can potentially destroy organic matter but their activity is minimal (Oremland et al., 1988). Alkaline waters have higher concentrations of dissolved CO<sub>2</sub> and P thereby favouring high productivity (Kelts, 1988). Clearly the combination of high productivity and excellent preservational conditions favours the accumulation of H-rich organic matter in alkaline lakes.

The influence of sedimentation rate on the quality of lacustrine source rocks is unclear. High clastic influx will probably favour organic C preservation (cf. Section 6.3) and the associated high influx of nutrients will foster high productivity (Powell, 1986). However, dilution of the aqueous organic matter by clastic influx combined with the lowering of the overall HI values by a TOM component will tend to decrease source rock quality (Katz, 1988). It is noteworthy that the Green River Formation, one of the best known lacustrine source rocks, accumulated in an arid climate with little clastic influx.

The distinctive chemical conditions of lakes ensures that they are readily identified in the geological record; their biomarker signature is particularly diagnostic (Volkman, 1988). Nonetheless, facies models for some ancient lakes are contentious (Section 8.3).

#### 7.4.2 Lagoons

Productivity is commonly high in lagoons leading to the development of oxygen-deficient conditions in the bottom waters. Kirkland and Evans (1981) have noted that, in particular, meso-to hypersaline lagoons are particularly favourable sites for black shale formation. They further consider that the circulation patterns observed in these lagoons (Fig. 7.5) can be used as an analogue for the much larger, silled embayments of epicontinental seas where the majority of Middle East source rocks apparently formed.

Mesosaline lagoons and embayments are favourable sites for black shale formation because of their high productivity, the lack of clastic dilution, and (probably most importantly) the virtual absence of sulphatereducing bacterial activity at high salinities. Due to evaporation, the surface waters are being constantly replenished by marine waters thereby providing ample nutrients for phytoplankton. Although the surface waters increase in density as they become mesosaline they are unable to sink due to the generation of even more dense, hypersaline waters around the lagoon margin (Fig. 7.5). This model predicts a highly characteristic facies association of basin-centred black shales surrounded by evaporitic facies.

The Mediterranean is the best present-day example of a large, silled basin with a negative water balance (Demaison and Moore, 1980) but here the density contrast between surface and deep waters is substantially less. Thus oxygenated surface waters can sink to the basin floor. If the Kirkland and Evans' (1981) model is viable then silled basins can apparently form black shales under a variety of circulation regimes. Perhaps only in a narrow 'window' of conditions where a negative water balance is achieved but salinities do not exceed saturation point (i.e. the present-day Mediterranean) are oxic conditions seen in silled basins.

In summary, the present is certainly not a perfect key to the past for black shale formation. A silled basin model is probably appropriate for many ancient black



Fig. 7.5. Model for the formation of black shales in a silled basin with negative water balance inferred from the dyamics of mesosaline lagoons (Kirkland and Evans, 1981).

shales (e.g. Demaison and Moore, 1980) but the Black Sea is a far from ideal type example. It is both too large and too deep for direct comparison and the best black shale sediments of Unit 2 formed in the mid-Holocene in poorly understood conditions. Kirkland and Evans' (1981) other use of a silled basin analogue involves the scaling-up of a lagoonal model by several orders of magnitude. In contrast, upwelling zone black shales, for which we have plenty of modern examples, may have been rather rare in the past.

### Ancient examples of black shale deposition

The preceding chapter highlights the difficulties of interpreting conditions favourable for black shale formation even in examples from the recent past. Interpretation becomes even more difficult in the geological past where the greater diversity of black shale occurrences (e.g. Klemme and Ulmishek, 1991) only exacerbates problems. The following three sections summarize something of this spectrum of ancient black shale depositional environments and the lively on-going debates as to their origin.

#### 8.1 THE CENOMANIAN/TURONIAN OCEANIC ANOXIC EVENT—AN EXPANDED OXYGEN MINIMUM ZONE?

Following the drilling of Cretaceous marine sediments by the Deep Sea Drilling Project, it became apparent that, unlike the modern oceans, the Cretaceous oceans were host to a large amount of organic-rich deposition. Black shales are common throughout the Cretaceous (North, 1979), but Schlanger and Jenkyns (1976) highlighted two relatively short intervals of the Cretaceous, the Aptian/Albian and the Cenomanian/Turonian, when black shale deposition was extraordinarily widespread. Both intervals correspond to times of major sea-level rise. Schlanger and Jenkyns coined the term oceanic anoxic event (OAE) and they suggested that much of the black shale deposition was due to the intensification and expansion of the oxygen minimum zone (OMZ) at times of heightened primary productivity.

The Cenomanian/Turonian example is the most extensive of these OAEs and can be considered as the type example of the phenomenon. Black shales formed over large areas of the North, Central and South Atlantic during this interval (Fig. 8.1). Organic-rich strata also accumulated in the equatorial Pacific on the flanks and tops of several seamounts such as the Shatsky Rise, Hess Rise, and Magellan Rise (Schlanger and Jenkyns, 1976).

Varied lithologies are associated with the OAE although all have elevated TOC values compared with their interbedded sediments. The most organic-rich sediments occur on the eastern margins of the Atlantic and along shelf margins (Jenkyns, 1985; Graciansky *et al.*, 1986). Many of the Atlantic black shales contain specimens of the benthic bivalve *Inoceramus*, indicating that depositional conditions were commonly dysoxic rather than truly anoxic (Thiede and van Andel, 1977). In the more expanded Atlantic sections black shales rhythmically alternate, on a 25 cm scale, with greenish-grey burrow-mottled mudstones (McCave, 1979) indicating fluctuating benthic oxygen levels. Around the western Tethyan margin there is only a modest organic enrichment associated with the Cenomanian/Turonian Bonarelli Horizon—a phosphatic, radiolarian siltstone (Arthur and Premoli Silva, 1982).

The broad premise of the Cenomanian/Turonian OAE has become widey accepted and it is now established as the type example of this phenomenon (e.g. Tissot *et al.*, 1980; Arthur *et al.*, 1984; Graciansky *et al.*, 1986; Schlanger *et al.*, 1987; Jacquin and Graciansky, 1988; Crumiere *et al.*, 1990). Several lines of evidence support Schlanger and Jenkyns' (1976) original hypothesis of deposition from a productivity-intensified OMZ:

(1) Black shales are best developed and persisted for longest on the eastern side of the Atlantic, consistent with deposition from an intensifed OMZ produced by coastal upwelling.

(2) The frequent association of radiolaria with Cenomanian/Turonian sediments is characteristic of highly productive surface waters.

(3) The preferential occurrence of black shales in mid-water rather than deep water settings is again typical of OMZ deposition (Thiede and van Andel, 1977; Arthur *et al.*, 1987).

(4) The presence of black shales on Pacific seamounts such as the Hess Rise (Arthur *et al.*, 1984). Early work originally appeared to indicate that black shales accumulated on seamounts over a prolonged period of the Cretaceous but more precise biozonation has indicated that the black shales actually accumulated during a series of relatively brief events, commonly associated with intervals of sea level rise (Sliter, 1989).

Our knowledege of the OAE has increased considerably since Schlanger and Jenkyns' seminal paper. The truly global nature of the event was confirmed by Scholle and Arthur's (1980) carbon isotope analyses of



Fig. 8.1. Global extent of oxygen-restricted deposition during the Cenomanian/Turonian boundary interval.

pelagic carbonates which showed a positive excursion across the Cenomanian/Turonian boundary. This is attributed to the widespread removal of isotopically light organic C into black shales at this time. The event can also be traced into epicontinental seas where extensive black shales in the US Western Interior and the North Sea appear to be synchronous with the oceanic occurrences (Graciansky *et al.*, 1986; Wright, 1987). Further evidence for the nature of the OAE can be gauged from the mass extinction which affected many marine invertebrates at the end of the Cenomanian (Vogt, 1989). This is illustrated by the sequential extinction of first deep- and then shallower-water planktonic foraminiferans. This appears to record the gradual upward expansion of harmful, oxygen-poor waters during the course of the OAE (Jarvis et al., 1988; Leary et al., 1989).

Schlanger and Jenkyns originally suggested that the OAE spanned the 14 million years of the Cenomanian and Turonian stages, but subsequent estimates have considerably shortened the duration of the event. Black shales formed more or less continuously in a few Atlantic basins (the Angola and Cape Verde Basins) from the Cenomanian to the Santonian (Graciansky *et al.*, 1986; Jacquin and Graciansky, 1988), but the wide extent of black shale deposition that characterized the OAE (Fig. 8.1) lasted for only a million years or so in the oceans (Arthur *et al.*, 1987) and as little as 100 000 years in some epicontinental seas (Gale, 1989). In the latter areas black shale deposition was initiated in the

deepest basin centres and expanded out onto the basin margins (e.g. Crumiere *et al.*, 1990)—an 'expanding puddle' of oxygen-deficient conditions (sensu Wignall, 1991a; cf. Chapter 9).

The beginning of the OAE coincides with the start of the positive carbon isotope excursion, the start of a major transgression, and the disappearance of the widespread planktonic foraminiferan *Rotalipora cushmani* (Hart and Leary, 1989). These events can be recognized in many regions but doubt has been cast upon their precise synchroneity by Bralower's (1988) nannofossil biostratigraphy. However, Gale *et al.* (1993) have shown, by detailed sampling of expanded basinal sections, that the so-called positive carbon isotope peak is actually a broad, positive plateau with subsidiary peaks superimposed upon it. The previous non-recognition of the several subsidiary peaks may have led to miscorrelation (Gale *et al.*, 1993).

The original OAE concept has been upheld by further research, but the causal mechanism remains the subject of debate. Initially, Schlanger and Jenkyns suggested that the transgression onto continental shelves caused an increase in the area of shallow productive seas. This, together with an equable climate 'which reduced the supply of cold oxygenated bottom water' (Schlanger and Jenkyns, 1976, p. 179) in the world's oceans, was held responsible for the OAE. The high productivity was attributed to the ample supply of nutrients from land areas during the transgression (Jenkyns, 1980; de Boer, 1982). However, virtually no clastic material was supplied to the seas during the latest Cenomanian transgression and it is difficult to envisage how a large supply of nutrients could occur independently of the riverine input.

An alternative cause of high productivity was derived from palaeoceanographic models of the Cretaceous world (Barron and Washington, 1982; Brass et al., 1982). In the absence of cold, polar waters in the Cretaceous it was suggested that evaporation in low latitude shelf settings created warm, saline bottom waters (WSBW). The present-day Mediterranean sources WSBW into the Atlantic, but it is of only minor significance compared to Antarctic bottom waters. During the latest Cenomanian transgression, the area of shallow shelf seas increased considerably, thereby increasing the generation of WSBW (Arthur and Premoli Silva, 1982). This increased rate of formation of WSBW would lead to more intense upwelling and therefore elevated productivity (Brass et al., 1982; Arthur et al., 1984; Schlanger et al., 1987; Hay, 1988). It should be noted that this revised model alters the site of maximal productivity from the shelves, as originally proposed (Jenkyns, 1980; de Boer, 1982), to the shelf margins (Fig. 8.2).

#### 8.1.1 Alternative models for the Cenomanian/ Turonian OAE

Ever since its first inception there has been considerable discussion of the cause of the OAE. Like many black shale debates this has polarized into productivity



Fig. 8.2. Model for the formation of Cenomanian/Turonian black shales. During transgression the increased area of shallow shelf seas causes the increased formation of warm, saline bottom waters (WSBW) and thus more vigorous oceanic circulation. This in turn causes enhanced upwelling and therefore the expansion and intensification of the oxygen minimum zone.

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versus preservation models (cf. Chapter 6). Thus Ryan and Cita (1977) have suggested that the Cenomanian/ Turonian black shales formed in silled basins where salinity stratification created favourable anoxic/dysoxic conditions for organic matter preservation—a model favoured by several subsequent authors (McCave, 1979; Waples, 1983; Stein, 1986; Zimmerman *et al.*, 1987; Bralower, 1988). In support of the model, Brumsack (1980, 1986, 1989) noted that trace metal enrichment patterns of Cenomanian/Turonian black shales are similar to those of the Black Sea, the type silled basin (Section 7.2), rather than those of sediments accumulating beneath modern upwelling zones.

The expected stratigraphic occurrence of black shales formed in silled basins is distinctly different from those formed during upwelling (Chapter 7). Initially black shales should form in the deepest areas of individual basins and gradually expand in extent as oxygen-deficient waters rise up through the water column (p. 66). This is the pattern seen in the epicontinental basins of the US Western Interior and the North Sea (Waples, 1983; Bralower, 1988) but the evidence from the Atlantic is more equivocal. Initially it was claimed that black shales began forming on the continental slope and shelf margin, as would be expected for productivity-induced oxygen deficiency (Schlanger and Jenkyns, 1976; Thiede and van Andel, 1977). Some subsequent authors considered that black shale deposition began in the deepest areas of the Atlantic and expanded upwards (Waples, 1983; Zimmerman et al., 1987). It is possible that the deep-water black shales represent resedimented organic-rich sediments transported downslope by turbidity currents (Summerhayes, 1981; Arthur et al., 1984; Graciansky et al., 1986; Katz and Pheifer, 1986). However, this process cannot be invoked if the onset of black shale formation in the deepest areas pre-dates that on the slopes. This is the case in the Angola and Cape Verde Basins at least, where black shales appear considerably earlier than the OAE (Graciansky et al., 1986). Clearly this debate can be resolved by the careful biostratigraphic dating of black shales from a variety of Atlantic sites.

A variant of the silled basin model has been proposed by Jeans *et al.* (1991) on the basis of their detailed and comprehensive geochemical study of the Cenomanian/Turonian boundary section at Dover, England. They noted that the stage boundary marks the onset of a prolonged cooling phase which, in association with a regression, produced a series of semi-isolated, temperature-stratified basins in which marine organic matter accumulated. The organic enrichment is considered to have been further aided by the increased flux of terrigenous organic matter into epicontinental seas during sea-level fall because, 'the oxidation of terrestrial organic matter could have caused temporary anoxia resulting in the enhanced preservation of marine organic matter ... '(Jeans et al., 1991, p. 629). This is a curious inference as, generally, terrestrial organic matter is rather unreactive, causing it to decay slowly and without creating a strong oxygen demand. Similarly, the suggestion of a regression at the Cenomanian/Turonian contradicts the majority of previous studies which indicate a major transgression at this time (e.g. Crumiere et al., 1990; Uličny, 1992). The evidence for regression is based upon analysis of a single locality which apparently shows that 'sea level (as judged by lithofacies) (Jeans, 1992, p. 369) was falling. However, whilst facies analysis is useful for palaeobathymetric estimates, regional stratigraphic studies are needed to determine relative sea-level changes. Small scale progradational (shallowing-up) episodes can readily occur within an overall transgressive interval.

In as much as there is any current consensus as to the cause of the Cenomanian/Turonian OAE, it appears that highly productive oceans occurred in the Atlantic whilst enhanced preservation was acting in epicontinental settings—a rather unsatisfactory and strangely coincidental combination of causes.

#### 8.2 THE KIMMERIDGE CLAY

The Late Jurassic of Europe witnessed a widespread and prolonged phase of black shale deposition, of which the Kimmeridge Clay is the most celebrated formation (Hallam and Bradshaw, 1979). Unlike the Cenomanian/Turonian black shales, this 'anoxic event' is entirely restricted to epicontinental and shelf settings located principally in a series of grabens and basins formed during a Kimmeridgian phase of rifting (Fig. 8.3). Both the Tethyan and Atlantic Oceans were fully oxygenated during the Late Jurassic and a variety of organic-poor mudstones and limestones accumulated (Winterer and Bosellini, 1981; Ogg et al., 1983).

The Kimmeridge Clay has been the subject of intense study since its recognition as the principal source rock of North Sea oil (Fuller, 1975). Much of this study has focused upon the readily accessible onshore outcrops which are not, in fact, that closely comparable in either age or facies type to the more poorly known offshore Kimmeridge Clay. In North Sea stratigraphy the Kimmeridge Clay consists of organic-rich shales characterized by high values of authigenic U which give it a 'hot shale' signature on gamma-ray logs (Thomas *et al.*,



Fig. 8.3. Kimmeridgian palaeogeography of northwest Europe showing the extent of black shale deposition in the earliest Kimmeridgian and at the maximum extent of black shale deposition in the Eudoxus Zone. CG-Central Graben, LBM-London-Brabant Massif, MFB-Moray Firth Basin, MNSH-Mid North Sea High, NDB-Norwegian-Danish Basin, VG-Viking Graben, WB-Wessex Basin.

1985). Total organic carbon values generally do not exceed 15% with the highest values of both TOC and HI occurring within the depocentres. Organic particles mostly consist of amorphous organic matter probably of marine origin (Stow and Atkin, 1987; Miller, 1990).

The onset of Kimmeridge Clay deposition coincides with the development of a series of grabens (Badley *et al.*, 1984; Beach, 1984). Rifting began in the Oxfordian in the Viking Graben, with the first black shales forming in sites of maximal subsidence and gradually expanding their extent along the graben axes (Thomas *et al.*, 1985). Kimmeridge Clay black shales do not appear until almost the end of the Jurassic in the Central Graben (Fig. 8.4). Towards the margins of the grabens, the black shales are interbedded with sandy to silty turbidites and breccias commonly derived from submarine fault scarps (Stow and Atkin, 1987; Wignall and Pickering, 1993). Deposition became much more widespread in the Eudoxus Zone of the Kimmeridgian with black shales expanding from their basinal settings to onlap the graben footwalls (Rawson and Riley, 1982; Figs. 8.3 and 8.4). The Eudoxus event marks a major transgressive episode that can be traced from southern Europe to Greenland (Wignall, 1991c). As the transgression is superimposed upon a phase of syn-rift tectonics it probably represents a eustatic sea-level rise



**Fig. 8.4.** Stratigraphic range of Kimmeridge Clay black shales (horizontal lines) in selected basins of northwest Europe. EZ marks the Eudoxus Zone, a time of widespread onlap of black shales. All columns depict a transect from basin centre (left-hand side) to basin margin (right-hand side). Stages are after their North Sea usage but note that the Kimmeridgian Stage of onshore Britain is of longer duration and includes the early part of the Volgian. After Dore *et al.* (1985), Thomas *et al.* (1985), and Wignall (1991c).

rather than post-rift onlap of the basin margins (Dore *et al.*, 1985). The extent of black shale deposition contracted during the latest Jurassic, although in the main grabens (the Viking and Central Grabens) hot shales persist up into the Ryazanian whereupon they are abruptly succeeded by organic-poor marks throughout the area (Fig. 8.4).

Onshore, the Kimmeridge Clay follows the same 'rules' as the North Sea with black shales appearing first in the local depocentres and becoming vastly more extensive in the Eudoxus Zone (Wignall and Hallam, 1991). Throughout the middle part of the formation depositional conditions were remarkably uniformmore so than at any other time in the Jurassic of England-and many individual beds can be traced over the entire outcrop (Gallois and Medd, 1979; Herbin et al., 1991b; Wignall, 1993b). The area of black shale deposition contracted in the early Volgian and again became restricted to basinal areas. The black shales were ultimately replaced by peritidal, semi-arid carbonates throughout the region (Francis, 1983). Clay mineral and other data indicates that the transition from a humid to semi-arid climate occurred whilst black shales were still forming in the depocentres of southern England (Wignall and Ruffell, 1990).

In contrast to the monotonous development of black

shales in the North Sea, the onshore Kimmeridge Clay exhibits fine-scale rhythmic deposition (Fig. 8.5). The rhythms consist of alternations of mudstones with organic-rich shales and occasionally coccolith limestones (Section 3.6; Gallois and Medd, 1979; Cox and Gallois, 1981). Organic C values are exceptionally high with up to 50% TOC occurring in the shales, whilst even in the more organic poor mudstones TOC levels may reach 10% (Tyson, 1989). There is generally little compositional variation of the organic content and Type II kerogens occur in all lithologies. This consists mostly of amorphous organic matter (AOM) in most samples (Williams and Douglas, 1983; Ebukanson and Kinghorn, 1985; Nohr-Hansen, 1989) with the addition of lamellar alginite in the most organic-rich shales (Williams, 1986; Tyson, 1989). Thus the TOC variations within the rhythms mainly record variations in the amount, rather than the composition, of the organic matter.

Evidence from palaeoecology (Section 3.6) indicates that the shales accumulated in more-or-less persistently anoxic bottom waters. However, the mudstones formed beneath persistently dysoxic bottom waters that enabled the sediments to be thoroughly burrowed. These differences appear to have had an effect on the state of preservation of the organic matter because, as



Fig. 8.5. Rhythmic alternations of black shales and mudstones in Cuddle Cliff, east of Kimmeridge Bay, southern England. Cliff height approximately 35 m.

Tyson (1989) notes, the AOM is more poorly preserved in the mudstones. However, his observation is contradicted by Tribovillard and Desprairies (1992) who note little variation in the preservational styles of the macerals between lithologies. In an important contribution to this debate, Bertrand et al. (1989) observed, using EDS multi-element mapping, that the organic C of the shales occurred both as AOM macerals and as diffuse, unfigured C in the mineral matrix where it is probably associated with organo-clay complexes (Ebukanson and Kinghorn, 1990). The latter component of the organic C is absent from burrowed areas presumably because it is ingested by the burrowing organism. Within the mudstones the larger macerals are preserved but, in this intensely microburrowed lithology, the diffuse organic C is almost totally absent. It is clear from these observations that the degree of burrowing (and therefore the levels of bottom-water oxygenation) had a strong control on levels of organic enrichment in the Kimmeridge Clay.

#### 8.2.1 Productivity models

Although of only minor importance in the Kimmeridge Clay, the presence of coccolith limestones has exerted a somewhat disproportionate influence on proposed depositional models. Gallois (1976) noted that the virtually monospecific coccolith flora was typical of modern eutrophic blooms. He therefore suggested that the limestones and organic-rich shales were the product of temporary high-productivity events that produced short-lived bottom-water anoxia. However, subsequent geochemical and palaeoecological analyses have shown that benthic conditions were characterized by longlived benthic anoxia (e.g. Wignall and Myers, 1988). High productivity is still favoured as a causal mechanism for anoxia by several authors (Aigner, 1980; Tribovillard and Desprairies, 1992). However, Farrimond et al. (1984) have shown that TOC variations do not vary with terrigenous organic matter input (which is only a very minor component of the total organic matter content). Some relationship would be expected if fluvially derived nutrient input (for which TOM input is regarded as a proxy) was controlling productivity variations.

#### 8.2.2 Preservation models

The Kimmeridge Clay coccolith limestones are closely comparable with Unit 1 of the Black Sea (Section 7.1). Thus, Tyson *et al.* (1979) proposed their deposition from beneath a permanently temperature-stratified water column where nutrient mixing from the monimolimnion into the mixolimnion triggered coccolith blooms. The organic-rich shales are inferred to have formed beneath a slightly lower stand of the thermocline. Most authors favour a maximum depth of around 50 m (Aigner, 1980; Hallam, 1987; Oschmann, 1988b; Miller, 1990), as suggested by the occasional presence of storm beds (Oschmann, 1988b; Wignall, 1989) considerably shallower than those encountered in the Black Sea.

Tyson's model is supported by much geochemical and palaeoecological evidence and it has been adopted in several subsequent studies (Hallam, 1987; Tyson, 1989; Wignall, 1989; Wignall and Hallam, 1991). For example, the coccolith limestones record the most intense and persistently anoxic conditions (Wignall, 1991b). Furthermore, the initial basin-centred development of black shales followed by their gradual concentric increase in extent is characteristic of deposition beneath an upward-expanding density interface (Wignall and Hallam, 1991).

#### 8.2.3 Palaeoceanographic models

Some authors have been impressed by the great lateral extent of Kimmeridge Clay deposition which has led to proposals of circulation models more akin to those encountered in oceanic settings. Thus, Oschmann (1988b, p. 235) stated that, 'the widespread nature of Kimmeridge Clay facies on the northwestern European shelf [epicontinental sea] and the established marine conditions from the Central Atlantic and Tethyan Ocean to the Arctic Ocean during Kimmeridgian time clearly contradict the land-locked silled basin model.' No one has suggested that the seas were 'land-locked' and this is not a requisite condition for Tyson's model. Also, Kimmeridge Clay deposition spanned the entire Oxfordian to Ryazanian interval (Fig. 8.4) but presumably Oschmann regards the silled basin model as inapposite for all examples of this facies. As an alternative, he proposes a 'North Atlantic water passage model' founded upon his predictions for late Jurassic climate. He suggested that, during summer months, cold Arctic waters upwelled onto the northern European shelf margin. This current flowed southwards, as a dense bottom current, along the Viking and Central Grabens to southern England whilst becoming deoxygenated along the route. Around southern England this deep water then became incorporated into a northward-flowing counterflow of warmer, less dense surface waters (Fig. 8.6). The temperature-stratified water column was broken down in winter due to a predicted decline in Arctic upwelling.

Elegant though Oschmann's model is, it is not supported by several aspects of Kimmeridge Clay stratigraphy. Even during the Eudoxus Zone event black shales were restricted to two distinct regions, a broad area of England and in the Viking and Moray Firth Grabens but not in the intervening Central Graben area (Dore *et al.*, 1985; Fig. 8.3). Therefore black shales were never deposited along the entire proposed passage route. Miller (1990) further argued that the cold Arctic waters would be highly oxygenated and he noted that an Ekman transport effect would have deflected the polar bottom currents along the coastline of East Greenland rather than along the North Sea grabens.

Miller (1990) has noted that Kimmeridge Clay faunas are generally of a northerly affinity, implying surface water currents flowing to the south. With this and other evidence he proposed a negative water balance for the north-west European basins in which evaporation generated warm saline bottom waters (WSBW) whilst southerly flowing, cold surface waters counterbalanced the evaporative loss (Fig. 8.7). Basinal areas therefore contained isolated, unmixed puddles of water that rapidly became anoxic. The proposed temperature profile of the water column in Miller's model is the inverse of that predicted by both Oschmann (1988b) and the proponents of the silled basin model (e.g. Tyson, 1989). Unfortunately oxygen isotope ratios cannot be used to distinguish between the models because ratios for cold water are essentially the same as for warm waters with slightly elevated salinity.

Miller's model accounts for many aspects of the Kimmeridge Clay but notably not the palaeoclimatic variations. The Late Jurassic of Europe witnessed a transition from humid to semi-arid climates with semiaridity gradually spreading northwards during the course of the Kimmeridgian and Volgian (Wignall and Ruffell, 1990). In southern England, where the climatic transition is recorded within the early Volgian, most of the exceptionally organic-rich shales accumulated prior to this time in a humid climate, whilst an arid climate is needed in order for evaporation and southward-flowing surface waters to be formed.



Fig. 8.6. Oschmann's (1988b) North Atlantic water passage model for the formation of Kimmeridge Clay black shales. Abbreviations as in Fig. 8.3.



Fig. 8.7. Miller's warm, saline bottom water model. Essentially this is the silled basin model, first proposed for the Kimmeridge Clay by Tyson *et al.* (1979), but with salinity rather than temperature-induced stratification. Abbreviations as in Fig. 8.3.

#### 8.3 THE GREEN RIVER FORMATION

The lacustrine facies of the Eocene Green River Formation contain some of the most celebrated, hydrogen-rich black shales (generally called oil shales) of the geological record. Initially they were the focus of a lifetime's study by W.H. Bradley (1966) and over the last two decades an increasingly large number of geologists have added to his exemplary work and stimulated a large debate on the origin of the oil shales. A remarkably diverse range of depositional conditions have been proposed for the lacustrine facies with suggested water depths ranging from tens of metres (perennial lake model) to millimetres (playa lake model). The variety of interpretations undoubtedly stems from the potentially rapid changes in lake level caused by subtle changes in run-off and evaporation.

The Green River Formation forms the approximately 1 km thick infill of Lake Gosuite that was situated in north-east Utah and western Wyoming for four million years of the Eocene (Eugster and Surdam, 1973). The formation is divided into three members; from base to top the Tipton, Wilkins Peak, and Laney Members (Fig. 8.8). Oil shales occur in all the members, although in considerably different facies associations. Thick, moderately organic-rich shales occur in the Tipton Member in association with dolomitic mudstones and sandstones, whilst thinner, but very organic-rich oil shales are interbedded with sodium salts (trona) in the Wilkins Peak Member (Eugster and Surdam, 1973; Smoot, 1983). The thickest and most organic-rich oil shales are found near the base of the Laney Member where they



**Fig. 8.8.** Lithostratigraphic section through the Green River Formation. After Eugster and Surdam (1973) and Fischer and Roberts (1991).

occur interbedded with stromatolitic limestones and dolomite (Fischer and Roberts, 1991). For many horizons the term oil shale is rather a misnomer, kerogen-rich, laminated carbonates are typical of the Laney Member whilst dolomites with kerogen laminae occur in the Wilkins Peak Member (Eugster and Surdam, 1973; Cole and Picard, 1975). The origin of the lamination has been the subject of considerable debate (cf. Section 2.4).

Green River oil shales are closely comparable with the sediments found in many modern-day, permanently stratified (meromictic) lakes (Bradley, 1929; Dickman, 1985). Bradley and Eugster (1969) therefore suggested that the oil shales accumulated in the deepest waters of a large, perennial, salinity-stratified lake in which anoxia developed in the bottom waters due to the inhibited advection of oxygen. The hegemony of this model was short-lived for Eugster and Surdam (1973) proposed, on the basis of desiccation cracks and breccias in the oil shales, that a playa lake model was more appropriate for the Wilkins Peak Member at least (Fig. 8.9). It was suggested that, 'oil shales accumulate[d] from organic remains ... brought into the lake from the playa fringes by flood' (Eugster and Surdam, 1973, p. 1118); the interlaminated dolomite layers were similarly said to be derived from the evaporitic flats

fringing the shallow, ephemeral lakes. Bradley (1973) concurred with this re-interpretation to some extent as he considered that occasional desiccation and 'mummification' of algal ooze formed in shallow lakes could be a factor causing the exceptional preservation of the lipidrich organic matter. In fact, the combination of high salinity and alkaline conditions implied in the playa lake model may have been sufficient to retard the normal bacterial breakdown of lipids.

As many of the supposed desiccation features of the Wilkins Peak Member also occur in the Tipton oil shale (mudcracks, loop bedding, injection features), the playa lake model was also proposed for this lower unit (Surdam and Wolfbauer, 1975). The reinterpretation was complete with Surdam and Stanley's (1979) study of the Laney Member, although here it was suggested that the absence of dolomitic laminae in the oil shales indicated that extensive fringing mud flats were not developed during their deposition. However, the shales are frequently capped by dolomites with saline mineral casts. An environment fluctuating between perennial meromixis (oil shales) and playa lake (dolomites) was therefore inferred.

By the early 1980s, 'The pendulum of changing opinions had swung to the point at which the existence of large [meromictic] lakes was questioned...' (Fischer



Fig. 8.9. Models for the formation of Green River Formation oil shales. Top: Playa lake model (e.g. Eugster and Surdam, 1973). Bottom: Perennial/meromictic lake model (e.g. Boyer, 1982).

and Roberts, 1991, p. 1146) but from this point it began to swing back again. The Green River oil shales contain many horizons with exquisitely preserved fish of freshwater types in sediments containing saline mineral casts (Boyer, 1982). This apparently conflicting evidence is best reconciled by a stratified water column model with low-salinity surface waters overlying briney deep waters (Fig. 8.9); this is Bradley's original meromictic lake. The association of oil shales and trona in the Wilkins Peak Member can be explained by a change from open to closed lake conditions perhaps triggered by an increase in aridity (Boyer, 1982). Boyer's assertions were supported by Smoot's (1983) detailed correlation exercise on the Wilkins Peak Member which showed that the oil shales formed during lake highstands whilst evaporites formed when the lake was shrinking. During the highstand intervals the area of evaporitic marginal flats was at a minimum, thereby provoking the question as to the origin of the dolomite laminae in the oil shales. Smoot (1983) suggested that the dolomite is a late-stage diagenetic replacement of calcite.

The desiccation features of the oil shales have also been the subject of reinterpretation. The polygonal cracks have been alternatively ascribed to synaeresis of cyanobacterial mats (Smoot, 1983). It is noteworthy that most of the desiccation phenomena (loop structures, injection features, oil shale breccias) of the Green River Formation oil shales also occur in Kimmeridge Clay oil shales (Wignall, 1989), an undoubtedly deep marine formation. Such features are probably a result of dewatering of exceptionally organic-rich strata without any evaporitic connotations.

# Transgressive black shales—a stratigraphic enigma

#### 9.1 THE TRANSGRESSIVE BLACK SHALE PROBLEM

The stratigraphic occurrence of black shales is an important, but often neglected, aspect of their study. Nonetheless many aspects of black shale stratigraphy can provide important evidence for evaluating competing models. However, the frequent association of source rocks with the early part of transgressive sedimentary cycles has posed one of major stratigraphic enigmas of the past few decades (Bitterli, 1963; Hallam, 1967b; Wignall, 1991a). Such stratigraphic associations are not restricted to the Phanerozoic as many Proterozoic black shales also occur within the transgressive part of sequences (e.g. Jackson and Raiswell, 1991).

Commonly source rocks directly overlie unequivocally shallow-water sediments such as coals (Heckel, 1977; Baird and Brett, 1991b; Coveney *et al.*, 1991), estuarine sediments (Leckie *et al.*, 1990), and even aeolian sands (Bell *et al.*, 1979), although evidence for the interdigitation of black shales with such facies is commonly lacking. Rather the shales rest on discontinuity surfaces that are commonly mantled by a thin layer of coarse material including bones, phosphatized faecal pellets, and sometimes glauconite (Bitterli, 1963; Gutschick and Rodriguez, 1979; Leckie *et al.*, 1990).

Many of the world's best source rocks belong to the transgressive black shale category (Creaney and Passey, 1993), with organic facies AB being typical (Huc, 1988). Marine, rather than terrestrial matter, tends to dominate the organic matter fraction (prasinophyte algae are particularly characteristic), whilst amorphous organic matter is the typical maceral (Grabowski and Glaser, 1990; Leckie *et al.*, 1990, 1992; Pasley *et al.*, 1991; Gregory and Hart, 1992).

To many authors the association of black shales with shallow-water facies and their stratigraphic occurrence in the early stages of sea-level rise has suggested a shallow-water origin (Hallam, 1967b; Leckie *et al.*, 1990; O'Brien, 1990; Banerjee and Kidwell, 1991; Coveney *et al.*, 1991; Hudson and Martill, 1991). Conversely, the common presence of a transgressive lag at the base of the black shales is held as evidence of a prolonged, sediment-starved phase of deepening implying a deep-water facies (Byers, 1977; Hallam, 1978; Elrick and Read, 1991; Wignall, 1991a; Wignall and Maynard, 1993). It is important to this debate to distinguish the implied palaeobathymetry. Thus, the 'shallow-water' epithet can infer that deeper-water facies are being deposited contemporaneously with the black shales (e.g. Leckie *et al.*, 1990; Banerjee and Kidwell, 1991; Hudson and Martill, 1991). Alternatively, black shales may be 'shallow water' in the sense that they are overlain by deeper water facies but they represent the deepest water facies accumulating at the time of their deposition. These alternatives are discussed further below.

An additional factor not always appreciated in the stratigraphic study of black shales is their precise position within the transgressive record. Many black shales rest on erosive or hiatal surfaces (discontinuity surfaces) where they mark the initial stages of transgression (Hallam, 1967b, 1978; Baird, 1976; Byers, 1977; Leckie et al., 1990; Elrick and Read, 1991). More commonly, black shales occur at the peak of transgression at the time of maximum shoreline retreat (Watney 1985; Graciansky et al., 1992; Leckie et al., 1992). In this situation they represent the condensed section associated with the maximum flooding surface of the Exxon stratigraphic model (Loutit et al., 1988; Creaney and Passey, 1993). Source rocks are also known from the early part of the highstand, following maximum flooding (Savrda, 1991; Curiale et al., 1991). In fact it has only been appreciated recently that two distinct types of transgressive black shale may be present in the stratigraphic record (Mavnard et al., 1991; Bisnett and Heckel, 1992; Wignall and Maynard, 1993). Before discussing this further, and in order to place these transgressive black shales in their stratigraphic context, the nature of the transgressive record is first reviewed.

#### 9.2 THE SEQUENCE STRATIGRAPHY OF TRANSGRESSIONS

Over the last decade or so the nature of the sedimentary record has been encoded in a sequence stratigraphic

model developed primarily by researchers at Exxon Production Research (EPR). In essence, the EPR model visualizes the sedimentary record to consist mostly of small-scale aggradational/progradational cycles or parasequences. The parasequences are grouped into several systems tracts each of which has a distinct stacking pattern (Van Wagoner *et al.*, 1990). Subsidence, sediment influx, and eustatic sea-level change all control the timing and development of the systems tracts, although sea-level variations are considered to be the principal control (Posamentier *et al.*, 1988), particularly in stable epicontinental settings.

The transgressive sedimentary record is typically very thin, and only in areas of high sediment influx are expanded transgressive system tracts seen. For example, large areas of the present-day continental shelves are covered in a thin veneer of reworked, relict Pleistocene sediments following the Holocene sea-level rise (Carter et al., 1991). At least two distinct mechanisms may be responsible for the sediment-starvation of shelf areas during transgression. Sea-level rise causes the drowning of river valleys and embayment of coastlines producing estuaries which trap sediment. An extensive sediment-starved transgressive surface therefore develops in shelf areas. Jervey (1988, p. 65) therefore noted that '[thin horizons of] Glauconitic sands, phosphorites, and organic-rich shales in the geologic record may indicate periods of rapid accommodation increase due to rapid eustatic sea-level rise, when most clastics were stored in coastal-plain and shoreline facies." Accommodation is the space between the sea floor and base level in which sediment can accumulate. The rapid increase of water depth inferred by Jervey implies that the organic-rich shales are considered to be a sedimentstarved, deep-water facies that are laterally equivalent to thick shoreline facies.

Another mechanism for the generation of sedimentstarved conditions again relates to the rapid generation of accommodation space during sea-level rise. Type 1 sequence boundaries, in the EPR model, are produced by rapid rates of sea-level fall in which base level drops below the shelf break causing the incision of a fluvial drainage network into the shelf. As base level begins to rise the incised valleys are gradually infilled until a point is reached whereby the drowning of interfluve areas creates a vast amount of new accommodation (Fig. 9.1). If sediment influx remains constant much of this new space remains unused and an extensive transgressive surface is developed that marks the base of the transgressive system tract. More minor (type 2) sequence boundaries do not extend beyond the shelf break and they are not associated with fluvial incision of the shelf. Therefore interfluve drowning does not occur during



Fig. 9.1. Strike section along a mid-shelf transect showing the increase in accommodation during three increments of sea-level rise spanning the transition from lowstand to transgressive system tracts. The drowning of the interfluve areas between the incised valleys creates a large volume of accommodation space leading to the development of a sedimentstarved transgressive surface (Posamentier and Vail, 1988).

sea-level rise with the result that transgressive system tracts are likely to be thicker and better developed.

Within the transgressive system tract small scale progradational episodes may be recorded by parasequences but each successive parasequence steps back towards the basin margin. The retreat of the parasequences is marked by an erosive surface that records the locus of the lower shoreface erosion point-this is termed the ravinement surface (Nummedal and Swift, 1988; Fig. 9.2). As the parasequences retreat towards the basin margin sediment-starved conditions typical of the basin centre gradually expand across the shelf. The peak extent of such conditions produces the maximum flooding surface. This is associated with a thin, condensed section in which sedimentation rates are initially exceptionally low (less than 1 cm/1000 yrs) and gradually rise as the overlying highstand systems tract is developed. Thus, in well developed transgressive system tracts three different type of erosive or hiatal surfaces are developed-transgressive, ravinement, and maximum flooding surfaces (Fig. 9.2).

In areas where sediment influx is low the transgressive system tract may become vanishingly thin and the sequence boundary, transgressive surface, and maximum flooding surface may all become amalgamated into a single major erosive/non-depositional surface. This is particularly common in the interfluve areas of sequences developed above type 1 sequence bounda-



Fig. 9.2. Sediment architecture of a well developed transgressive system tract showing the range of erosion surfaces associated with a retrogradational parasequence set.



Fig. 9.3. Strike section along a mid-shelf transect showing the lateral variability of the transgressive record caused by the lateral variability of sediment influx.

ries (Fig. 9.3). As noted in Section 9.1, transgressive black shales commonly overlie disconformities, but distinguishing the type of surface they represent in the EPR model requires detailed mapping. As there have been few attempts at such analysis for black shalebearing sequences, the following section documents a series of case studies based on examples from the British Carboniferous and Jurassic.

#### 9.3 EXAMPLES OF TRANSGRESSIVE BLACK SHALES

### 9.3.1 Marine bands of the Late Carboniferous of northern England

The Late Carboniferous (Namurian and Westphalian Series) of the British Isles consists of a succession of

cycles of mudrocks and fluviodeltaic sandstones, called cyclothems (Ramsbottom, 1977). The high frequency of the cyclothems implies a cause related to Milankovitchdriven climatic changes of which glacioeustatic sea-level changes are the most popular (Maynard and Leeder, 1992). The principal hinterland lay to the north and north-west of England where a Caledonian mountain chain was undergoing rapid erosion and supplying large volumes of sediment. To the south of the principal depocentres an island, the London-Brabant Massif, supplied relatively little sediment but effectively isolated the water bodies to the north from marine conditions (Fig. 9.4). As a result, most Late Carboniferous deposition in northern England occurred in fresh or slightly brackish conditions. Marine conditions are only recorded from numerous thin black shales (marine



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Fig. 9.4. Palaeogeography of the British Isles during the Late Carboniferous. M and BH denotes the locations of Middlecliff and Bullhouse Quarries shown in Fig. 9.6.

bands) which contain a prolific and biostratigraphically useful fauna of goniatites and paper pectens. Organic enrichment is variable but commonly exceeds 10 wt % TOC (Maynard, 1991).

Marine bands are commonly enriched in trace metals (Spears and Amin, 1981), implying very slow sedimentation rates. They also commonly extend over large areas of the British Isles (Calver, 1968). Both attributes suggest that the marine bands are condensed sections associated with maximum flooding. However, recent detailed analysis of the topmost Namurian Gastrioceras cumbriense Marine Band has demonstrated that the transgressive record of these Carboniferous cyclothems can be considerably more complex.

The G. cumbriense Marine Band overlies the Lower Haslingden Flags, an elongate fluviodeltaic sandbody that prograded into the Rossendale-Huddersfield Basins from the west (Collinson and Banks, 1975). In the most westerly outcrops the Flags are capped by a palaeosol, marking subaerial exposure and abandonment of the delta. This presumably marks a sequence boundary, although it is a relatively minor example as no incision is recorded from this level (Maynard, 1992). The sandstone body exerted an influence on the deposition of the succeeding sedimentary cycle by acting as an elongate high in the centre of the basins upon which mudrock deposition gradually onlapped (Fig. 9.5).

In the thicker basinal successions, the basal part of the transgressive record consists of Owd Bett's Horizon, a distinctive black paper shale that sits sharply on a variety of lithologies. This remarkable horizon resembles a marine band both lithologically and geochemically but it does not contain the goniatites or other shelly fauna that characterize true marine bands (Maynard et al., 1991). However, the occurrence of palaeoniscid fish scales and high S/C values strongly suggest marine depositional conditions. Owd Bett's Horizon records the initial stages of transgression for it only onlaps the margin of the Lower Haslingden Flags and is restricted to the Rossendale-Huddersfield Basins. Over its outcrop it maintains both a uniformity of thickness and character with no evidence for lateral variation.

Siderite concretions occur in the shales overlying Owd Bett's apparently recording a return to nonmarine conditions. The onset of marine conditions once again is heralded by the loss of the siderite and the appearance of Lingula in shales which mark the base of the G. cumbriense Marine Band. A gradual salinity increase is recorded in the faunal succession in the basal few centimetres of the Marine band, culminating in a thick-shelled goniatite fauna developed in two black paper shales (Fig. 9.5; Wignall, 1987). The G. cumbriense Marine Band black shales extend beyond the Rossendale-Huddersfield Basins and cover a large area of northern England. At the margins of their distribution the black shales grade into a thicker succession of siltstones and ultimately sandstones. There is also a faunal change with the loss of goniatites and the appearance of a diverse benthic assemblage (Wignall, 1987). Thus the black shales represent a condensed section that becomes expanded in nearshore sections. Overrall, the G. cumbriense cyclothem contains a basal transgressive black shale and two widespread black shales developed during maximum flooding.

Marine bands continue to occur throughout the overlying Westphalian succession of which the Gastrioceras listeri Marine Band is one of the best developed and regionally most extensive example. Over most of its outcrop in northern England, the G. listeri Marine Band sits directly on a coal which in turn rests on a thick palaeosol—the section at Middlecliff Quarry in South Yorkshire is typical of most localities (Fig. 9.6). The lower half of the marine band consists of black paper shales with TOC values peaking at 16.5 wt % near the base. The fauna is dominated by goniatites and paper pectens, including the splendid *Dunbarella papyracea* which commonly cover bedding planes (Fig. 3.14).

#### Examples 91



Fig. 9.5. Correlation of sediments associated with the *Gastrioceras cumbriense* Marine Band in the Rossendale-Huddersfield Basins of northern England showing the interpreted bounding surfaces (cf. Wignall and Maynard, 1993).



Fig. 9.6. Lithology and palaeontology of the *Gastrioceras listeri* Marine Band at two quarry sections in South Yorkshire showing (inset) the detailed transgressive record at the base of the marine band (cf. Fig. 9.4 for locations).

Like the Owd Bett's Horizon, the G. listeri Marine Band black shales appear to rest on a transgressive surface which, in this case, caps a coal seam. However, detailed analysis of the base of the marine band reveals a very thin but nonetheless significant transgressive record prior to the onset of black shale deposition (Fig. 9.6). The basal-most millimetre of the shale contains abundant, comminuted plant fragments whilst the overlying two millimetres of shale is grey, rather than black, and contains thin-shelled goniatites and bivalves. Only at 3 mm above the base are black shales with thick-shelled goniatites developed.

At the nearby Bullhouse Quarry a similar succession of shales and faunas are developed in the G. listeri Marine Band but the basal black shale at this locality is underlain by 70 cm of grey shale with a diverse benthic fauna (Fig. 9.6). This locality is therefore exceptional in preserving a transgressive record that at other localites is only a few millimetres thick. The black shales are interpreted to rest on a maximum flooding surface rather than a transgressive surface, although at most localities, such as Middlecliff Quarry, the two are separated by only a few millimetres of shale.

The analysis of the G. listeri Marine Band emphasizes the need for both millimetre-scale logging and lateral control when studying transgressive black shales.

#### 9.3.2 The Grey Shale

In most areas of north-west Europe the boundary between the Pliensbachian and Toarcian Stages of the Early Jurassic is a sequence boundary that marks the base of a major Toarcian transgression (Jenkyns, 1985). Only in the Cleveland Basin of northern England is a complete succession developed across this interval. The Late Pliensbachian in this region is represented by the Cleveland Ironstone Formation which contains a variety of shallow marine facies, including oolitic ironstones, and diverse benthic assemblages (Hallam, 1967a). Half a metre from the top of the Formation a 15 cm thick, silt-laminated black shale (the Sulphur Band) sits sharply on a siltstone with a large and diverse benthic fauna (Fig. 9.7). The basal contact of the Sulphur Band may be a correlative conformity to a sequence boundary because, around the northern margin of the Cleveland Basin, several metres of strata are missing from beneath this level (Howarth, 1973, p. 246).

The Band derives its name from its appearance at outcrop caused by the weathering of its abundant pyrite content. The silt laminae towards the top of the Sulphur Band become gently undulatory and exhibit very low angle cross lamination along with broad scour-and-fill structures. Both pelagic and benthic fauna are absent, implying anoxic conditions extending from the sea floor into the water column but, curiously, the shales are not enriched in authigenic U, implying oxic conditions. Chondrites and Diplocraterion penetrate the top of the Sulphur Band and the overlying mudstones show vestiges of silt-lamination between the dense burrows of these two ichnogenera (Fig. 9.8). There is no sequential development of burrow types and so it would appear that Sulphur Band deposition was terminated by the sudden onset of fully oxygenated sea floor conditions. Diplocraterion is a dwelling burrow normally associated with shallow-water deposition and the diverse assemblage of thick-shelled benthic bivalves in the overlying silty mudstone add credence to such an interpretation.

A similar lithology to the Sulphur Band occurs around a metre higher in the succession in the base of the Grey Shales (Fig. 9.7). This silt-laminated black shale also rests on a sharply defined bedding plane (a flooding surface?) and again it contains no authigenic U. However, in this case there is no burrowing in the top surface and the presence of a few ammonites within the black shale indicates less intense oxygen deficiency in the lower water column.

The remainder of the Grey Shales are bioturbated and contain a modest diversity of benthic taxa. These accumulated during a phase of basin margin onlap (Wignall and Maynard, 1993). Thus the thin black shales at the base of the Grey Shales occur in a basal transgressive position in close association with shallow water facies.

#### 9.3.3 The Lower Oxford Clay

The final example of a transgressive black shale comes from the Middle Jurassic succession of England. The Oxford Clay was deposited during a Callovian transgression that saw the spread of mudrock deposition over a large area of the British Isles. Organic enrichment only occurs in the basal part of the succession in the well known Lower Oxford Clay, celebrated for its diverse and well preserved marine vertebrate fauna (Martill, 1985, 1987; Hudson and Martill, 1991). Peak TOC values occur in the Jason Zone at the base of the Lower Oxford Clay where the benthic fauna is also at its most impoverished (Duff, 1975). The mudstones of the succeeding Middle Oxford Clay are organic-poor and become carbonate-rich towards the top, culminating in the highly fossiliferous Lamberti Limestone with a distinctive deep-water gastropod fauna (Hollingworth and Wignall, 1992).

The sequence stratigraphy of the Oxford Clay in



**Fig. 9.7.** Boundary beds between the Cleveland Ironstone and Grey Shales Formations, Brackenberry Wyke, North Yorkshire. Karen Wignall sits on the transgressive surface at the base of the Sulphur Band whilst Kath Hinchliffe is standing on the flooding surface at the base of black shale.



Fig. 9.8. Chondrites and Diplocraterion burrows developed in the top of the Sulphur Band at Brackenberry Wyke. Coin is 2 cm in diameter.

eastern England once again demonstrates that organicrich shales form the basal part of transgressive system tracts (Fig. 9.9). Maximum flooding in this case probably occurs around the top of the Lamberti Limestone, the horizon of minimum terrigenous influx in the sequence. The northern margin of the Oxford Clay depocentre was formed by the Market Weighton High, a persistent positive structural feature throughout the Jurassic. The Lower Oxford Clay only onlapped the margin of this high and, at the feather-edge of its occurrence (e.g. Nettleton Bottom, Fig. 9.9), it rests unconformably on the top of the underlying Kellaway Beds.

#### 9.4 TYPES OF TRANSGRESSIVE BLACK SHALE

The above examples illustrate that two distinct types of black shale can occur within the transgressive sedimentary record: basal transgressive (BT) black shales (e.g. Owd Bett's Horizon, the Sulphur Band, and the basal part of the Lower Oxford Clay) and maximum flooding (MF) black shales (e.g. the black shales of the G. cumbriense and G. listeri Marine Bands).

BT black shales are distinguished by several features:

(1) They rest directly on a transgressive surface which may coincide with a sequence boundary or its correlative conformity as is probably the case with the Sulphur Band and Lower Oxford Clay examples.

(2) They are only developed in topographic hollows and basin-centre locations at times of non-deposition on the basin margin. Thus, as Grabowski and Glaser (1990) noted, BT black shales have no time-equivalent shoreline facies.

(3) They exhibit no lateral facies variation (perhaps implying pelagic depositional processes).

(4) They are probably a shallow-water facies, as they occur at the base of the transgressive system tract and, in the case of the Sulphur Band, they are directly and conformably overlain by shallow marine facies. However, at the time of their formation there are no time-equivalent deeper-water facies.

Sedimentation rates for BT black shales are difficult to evaluate; the enrichment of authigenic U in Owd



Fig. 9.9. Stratigraphy of the Callovian succession of eastern England based on the wireline logs of Penn et al. (1986).

Bett's Horizon may indicate slow rates but the lack of enrichment in the Sulphur Band may indicate the converse. Further geochemical data are available for transgressive black shales from the Late Carboniferous of the United States (Covency *et al.*, 1991) but these examples may include both BT and MF black shales (Bisnett and Heckel, 1992). It is not yet clear if BT and MF black shales can be distinguished geochemically from each other.

MF black shales can be diagnosed by the following stratigraphic features:

(1) They rest conformably on maximum flooding surfaces, although in those cases where the transgressive systems tract is poorly developed (it is only 3 mm thick in the G. listeri Marine Band example!), they may closely overlie transgressive surfaces and sequence boundaries.

(2) Although MF black shales may extend for considerable distances onto the shelf they ultimately pass proximally into thicker sections of shallower, marginal marine facies.

(3) They represent a deep-water, sediment-starved condensed section.

#### 9.5 MODELS FOR TRANSGRESSIVE BLACK SHALES

#### 9.5.1 Maximum flooding (MF) black shales

MF black shales represent the expansion of conditions normally only seen in basinal locations, and I have therefore proposed an 'expanding puddle' model for their formation (Wignall, 1991a; Fig. 9.10). This is a variant of the silled basin model (cf. Section 7.1) in which dysoxic/anoxic bottom waters are inferred to occur beneath a stratified water column. Support for this model comes from their 'bull's-eye' geographical occurrence implying that the black shales formed in deep-water settings. The great extent of such deepwater conditions is probably the result of a very rapid rate of sea-level rise at the inflexion point of the rising sea-level curve. Therefore, only in areas immediately adjacent to the sediment source was sedimentation able to keep pace with such a rapid rate of accommodation increase whilst over most of the depositional area water depths increased rapidly as sediment starvation occurred.

The nature of the water column stratification is open to speculation. A brackish surface layer is unlikely as the interval of maximum flooding marks a minimum of sediment influx to the basin and it is likely that freshwater runoff is also minimal at this time. Temperature stratification is commonly invoked with colder, denser bottom waters overlain by warmer surface waters (e.g. Byers, 1977; Watney, 1985; Heckel, 1991; Baird and Brett, 1991a). However bottom waters could also be both warmer and more saline than the surface waters (e.g. Miller, 1990). As noted in Section 8.2, it is not easy to distinguish between these two stratification styles in the geological record.

The presence of a pycnocline in the water column can exert an important control upon sedimentary processes. For example, by constraining turbidity currents to spread across such an interface, the fine-grained suspended load is deposited over a much broader area than would happen if the current maintained contact with the sea floor thereby reducing the sedimentation rate at any one site (cf. Section 2.2.2, p. 7). Baird and coworkers (Baird *et al.*, 1987; Baird and Brett. 1991a) also noted that the presence of internal waves flowing along the top of the pycnocline may cause erosion of the sea floor in advance of the onlapping black shale facies (Fig. 9.11). Thus MF black shales may rest on an



Fig. 9.10. Expanding puddle model for maximum flooding (MF) black shales.



Fig. 9.11. Internal wave erosion model after Baird and Brett (1991a) with the permission of the authors and the Geological Society. a, Black shales; b. concretionary limestone truncated by corrosion in dysoxic waters; c, reworked detrital pyrite; d. packstone veneer of pyrite-calcareous debris; e, living coral thicket; f. internal wavetrain impinging palaeoslope.

erosion surface which, in the type examples from the Devonian of New York State, is paved in pyritic and phosphatic material reworked from the underlying strata. Baird and Brett (1991b) have also recorded bone/pyrite/conodont lags from beneath Pennsylvanian black shales of the United States which they attributed to the same process of internal wave erosion.

Maximum flooding erosion surfaces are comparable to the ravinement surfaces encountered in the transgressive system tracts because they are time-transgressive and become younger towards the basin margin. They do not record a prolonged hiatus in deposition but merely the passage of internal waves and the pycnocline across the sea floor. It is important that these erosion surfaces are distinguished from transgressive surfaces (and sequence boundaries) in order that the correct stratigraphic occurrence of black shales is determined. In practice the two types of erosion surface should be readily identified as the internal wave erosion concentrates pyritic lags in oxygen-deficient waters (Fig. 9.11) whilst such material is unlikely to be preserved by the subaerial/shallow marine erosive processes recorded in a transgressive surface.

#### 9.5.2 Basal transgressive (BT) black shales

BT black shales are considerably more difficult to interpret in terms of the silled basin model. Their close interbedding with shallow-water facies clearly implies that they too formed in relatively shallow water. However, they accumulated in depocentre locations and there are no contemporary deeper- or shallower-water facies. The presence of local topographic hollows during the initial stages of transgression appears to be the crucial factor in the BT black shale formation when the 'individualisation of small basins' was important (Dabard and Paris, 1986, p. 26).

Hallam was the first to consider the importance of an irregular bottom topography for black shale formation because, as he recognized, 'These irregularities would have locally inhibited bottom [water] circulation and allowed isolated pockets of stagnant water to persist ... ? (Hallam and Bradshaw, 1979, p. 160). Renaming the 'pockets' as puddles, I have incorporated Hallam's irregular bottom topography model into a puddle model for BT black shales (Wignall, 1991a; Fig. 9.12). Other than the restriction of bottom-water circulation. such hollows would also have served as traps for finegrained sediment and organic detritus (Huc, 1988). Thus, bottom-water oxygen demand may have been high, further enhancing oxygen restriction (Tyson and Pearson, 1991). The conditions of early transgression are particularly favourable for the development of local sea-floor hollows due to the drowning of incised river valleys. Also, a low sediment influx could have caused the most rapidly subsiding depocentres to become accentuated. The latter process is probably relevant for the examples of BT black shales given in Section 9.3.

The puddle model successfully explains many aspects of BT black shales, but several enigmas remain. With the exception of the minor sediment content of the black shales themselves, there is a total absence of sediment input into the depositional basin at the time of their formation. This may be related to the shape of the sea-level curve. For the purposes of the EPR model, the sea-level curve is considered to be sinusoidal. However,



Fig. 9.12. Puddle model for basal transgressive (BT) black shales.

glacioeustatic sea-level curves for the Pleistocene appear to be distinctly asymmetric with rapid rises and slow falls recording the slow build-up and rapid melting of continental glaciers (e.g. Williams, 1988). Thus, exceptionally rapid initial sea-level rise could possibly cause all sediment input to be trapped in the lower reaches of floodplains at this time.

The cessation of BT black shale formation is equally puzzling. The few decimetres thickness of Owd Bett's Horizon and the Sulphur Band is unlikely to have been sufficient to have infilled the hollows, and some other cause must be sought for the sudden oxygenation seen above these horizons. In the Owd Bett's example, the cessation of black shale deposition is even more strange for it is succeeded by a freshwater depositional episode prior to the re-establishment of marine black shale deposition.

Several authors have suggested that the initial transgressive episode may be a time of exceptionally high organic carbon influx to the sea floor (Jenkyns, 1980; Dabard and Paris, 1986; Middelburg *et al.*, 1991; Bisnett and Heckel, 1992). However, this interval corresponds to a minimum in terrigenous clastic influx and therefore, presumably, a similar low point in nutrient supply.

In the end the evaluation of all the factors leading to BT black shale deposition must remain just one of the plethora of enigmas which combine to make black shales the most interesting of all sedimentary rock types.

## Appendix

Acronyms used in the text:

- AOM Amorphous organic matter
- BT Basal transgressive
- COR Carbon oxidation rates
- EPR Exxon Production Research
- MF Maximum flooding
- MOM Marine organic matter
- OAE Oceanic anoxic event
- OMZ Oxygen minimum zone

- ORB Oxygen-restricted biofacies
- ORI Oxygen-related ichnocoenosis
- RMB Rhoads-Morse-Byers model
- SAR Sediment accumulation rates
- TOM Terrestrial organic matter
- TOC Total organic carbon
- WSBW Warm saline bottom water

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