An investigation of the sediment dispersal operating to control lithofacies variability and organic carbon preservation in an ancient mud-dominated succession: a case study of the Lower Jurassic mudstone dominated succession exposed in the Cleveland Basin (North Yorkshire)

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Abstract

In this study the Cleveland Ironstone and Whitby Mudstone Formations have been investigated to characterise: a) the evolving mudstone facies present in a basin that is gradually deepening and developing bottom water anoxia over time and b) what the fundamental geological controls were on this variability.

Using detailed facies descriptions obtained from analyses of approximately 151 samples obtained from combined optical, electron optical and geochemical methods 6 lithofacies have been identified. These include: 1) sand and clay-bearing, silt-rich mudstones, 2) silt-bearing, clay-rich mudstones, 3) clay-rich mudstones, 4) clay, calcareous nannoplankton-, and organic carbon-bearing mudstones, 5) fine-grained muddy sandstones, and 6) cement-rich mudstones. Individually, the samples are highly heterogeneous and typically organised into thin beds (<10 mm thick). These beds contain varying proportions of materials derived from inputs to the basin, primary production within the basin and the effects of diagenesis. In addition, they are microtexturally diverse and preserve primary depositional textures such as: sharp bases, normal graded bedding, starved ripple laminae, triplet fabrics, tempestites, pelleted laminae as well as a variety of burrowing fabrics.

With these data three main questions were addressed (each of these questions forms the basis of a paper). These include (1) Identifying the main processes responsible for sediment dispersal in this succession, (2) Discussing the mechanisms of organic carbon preservation when bottom water anoxia was not as prevalent as most authors have assumed and (3) Determining if this succession can be interpreted within a sequence stratigraphic framework.

The presence of ripples and triplet fabrics throughout this succession indicate that mud-deposition in this succession was much more dynamic than most researchers had assumed. Moreover there was not that much difference between the processes operating to deliver and disperse sediment in the coarser parts of the succession compared with those operating in the finer grained, more production parts of the succession. The large volumes of organic carbon preserved here indicate that the role of bottom water anoxia as a pre-requisite for enhanced organic carbon preservation in sediments has been overstated. Moreover, the presence of marine snow suggests that much of the organic carbon was delivered episodically to the sea floor following phytoplankton blooms. Finally, as a significant fraction of the sediment is being dispersed by advective processes operating to infill available accommodation the building of sequences can be recognised (namely beds, parasequences, and systems tracts at stratal surfaces) this type of succession is reasonably interpreted using sequence stratigraphic principles.

This study demonstrates that it is possible to directly link up-dip lithofacies variability in proximal sandy-mudstone deposits with coeval variations down-dip in distal basinal deposits. There is no reason why the processes occurring in basinal settings should be disconnected from those occurring up-dip in the lower shore face and offshore transition environments as their deposition represents a continuum of processes.

Declaration

The author declares that no portion of the work referred to in the thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

Copyright Statement

Section 1:

Introduction and background

Chapter 1

Introduction and thesis outline

1.1. Introduction

Mud and mudstones (fine-grained sediments with an average grain size < 62.5 µm) are the most abundant (>60%) sediment and sedimentary rock types preserved close to the surface of the Earth (e.g. Potter et al., 1980; Blatt, 1982; Aplin et al., 1999; Potter et al., 2005; Aplin and Macquaker, 2010). They have been deposited throughout much of Earth's history and in many environments, including: lake basins, continental shelves, and ocean basins (e.g. Nittrouer and Wright, 1994; Aplin et al., 1999; Wright and Friedrichs, 2006; Walsh and Nittrouer, 2009; Aplin and Macquaker, 2010). Mudstone-dominated successions commonly contain the most complete stratigraphic record of any sedimentary rock type (e.g. Blatt, 1982). Detailed analyses of these sediments give us a better understanding of the depositional and diagenetic processes that were responsible for their formation. Some mudstones contain significant quantities of organic matter [>2% total organic carbon to be source rocks] and the environments in which they were deposited were major sites of ancient carbon sequestration (e.g. Tissot and Welte, 1984; Tyson, 1995). In petroleum systems organic carbon-rich mudstones are the source rocks for almost all the world's oil and gas (e.g. Pegrum and Spencer, 1990; Schieber, 1999, 2001; Durham, 2008). In addition, mudstones host many metalliferous resources such as silver, molybdenum, zinc, chromium and iron (e.g. Potter et al., 1980; Maynard, 1983). Moreover they also may be principal raw materials used in manufacturing many industrial products like porcelain, ceramics, and bricks (see also Potter et al., 1980).

Mudstones deposited in ancient shelf seas are particularly important as they are very common and significant components of many petroleum systems (e.g. in the North Sea, Saudi Arabia and Niger Delta) because they act both as sources of hydrocarbons, and seals to many hydrocarbon reservoirs (e.g. Klemme and Ulmishek, 1991; Charpentier et al., 1993; Roen and Kepferal, 1993; Bohacs et al., 2005). In spite of their importance the variability that they exhibit is usually not incorporated into basin-scale facies models as they are assumed to contain little diagnostic information (e.g. grain size, sedimentary structures) that allows them to be easily linked to updip facies variations (e.g. Van Wagoner et al., 1990).

Shallow (shelf) seas occur around continents and extend from coasts, where shoreline processes take place, to the upper margins of the continental slopes (e.g. Johnson and Baldwin, 1986; Reading, 1996; Nichols, 2009). The important characteristics of this environment are gentle slopes much less than 0.7° (e.g. Walsh and Nittrouer, 2009), normal marine salinities (between 3.1% and 3.8%), water depth less than 200 m (e.g. Johnson and Baldwin, 1986) and interaction of different physical processes (e.g. tidal currents, waves, and storm currents) as well as biological and diagenetic effects (Figure 1.1).

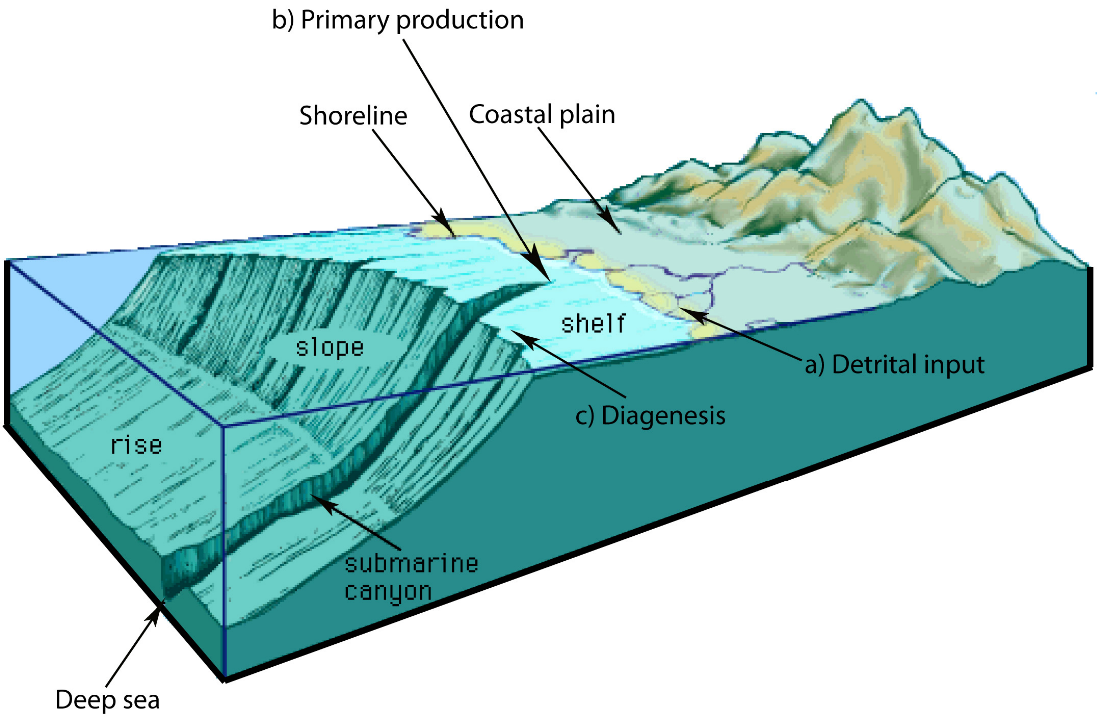

Figure 1.1. Schematic diagram illustrating the location of the continental shelf relative to slope and flood plains. This environment is: a) receiving detrital sediment and nutrients from fluvial run-off, b) receiving sediment from primary production in the water column, and exporting sediment down the canyon and c) undergoing diagenesis (both microbially-mediated and burial). (after Encyclopaedia Britannica, 1994)

Two main morphological types of shallow shelf seas are recognized (e.g. Johnson and Baldwin, 1986; Reading, 1996; Nichols, 2009): (1) pericontinental seas that occur on continental margins and are characterized by classic shoreline-shelf-slope profile where the stacking basins are controlled by either sediment supply or accommodation availability. (2) Epicontinental or epeiric seas (semi-enclosed basins) that form inland seas within continental areas and that are characterized by shallow water depth and typically have uniformly dipping ramp profiles.

Following these initial observations this study will focus on investigating mudstones deposited in ancient shelf seas, and aims to shed light on their origin, dispersal and their modification during early burial.

1.2. Rationale

Over the last four decades, there has been some attention given to how fine-grained sediments were deposited on ancient continental shelves. Researchers (e.g. Tourtelot, 1979; Aigner, 1982; Stanley, 1983; Macquaker and Curtis, 1989; Cheel and Leckie, 1993; Macquaker and Gawthorpe, 1993; Wignall, 1994; O'Brien, 1996; Macquaker and Howell, 1999; Taylor and Macquaker, 2000; Macquaker et al., 2007; Schieber et al., 2007) have studied ancient mudstones to determine from where their components were derived and how these constituents were transported around this environment. In spite of their common occurrence, however, relative to other rock types, they are poorly known. Klemme and Ulmishek (1991) proposed that the major difficulty with studying and interpreting fine-grained sediments lies in a lack of readily accessible analogues. Other sedimentologists (e.g. Oertel and Curtis, 1972; Weaver, 1989) noted, from their experience, that shales are hard to work with: because they are very fine-grained and unlike other sediment types lack obvious field and hand specimen-scale sedimentary structures. These characteristics have resulted in them being commonly studied using their hand-specimen scale appearance in combination with measured proxies (e.g. organic-carbon content, carbonate content, fossil content), that are used to generate descriptions to characterise these sediments. The nomenclature commonly used to describe the rocks includes terms such as: oil shale, gray shelly mudstone, and black organic- rich mudstone (e.g. Weaver, 1989; O'Brien, 1990, 1996; Wignall, 1994). Although these descriptions are adequate when fine grained sediments are being compared with facies present in sandstone- and limestone-dominated successions, they are not particularly useful as discriminators of either the different mudstone depositional environments or early diagenetic process where mudstones are the specific focus of study because their appearance is strongly influenced by weathering (see Macquaker and Gawthorpe, 1993; Macquaker and Adams, 2003). Therefore historically, work with shale has been given a low reward/investment ratio. Notwithstanding the above difficulties, scientists (including Potter et al., 1980; Aplin et al., 1999; Potter et al., 2005; Aplin and Macquaker, 2010) have proposed that shales deserve much more attention and, when properly studied, can yield valuable additional insight into the origins of the fill of many sedimentary basins.

1.3. Mudstone facies at basinal scales

Using geochemical and palaeontological proxies, coupled with their apparent laminated appearance in hand specimen scales to characterise mudstone variability in distal shelf environments most authors (see for example Didyk et al., 1978; Tourtelot, 1979; Demaison and Moore, 1980; Wignall, 1991, 1994; Sælen et al., 1995; Sælen et al., 2000; Stow et al., 2001; Wignall et al., 2005; Loucks and Ruppel, 2007) have argued that the main controls on lithofacies variability in these rocks are: varying bottom water oxygen concentrations, primary production and suspension settling. In contrast, in proximal muddy environments researchers (e.g. Hourbolt, 1968; McCave, 1969, 1971; Fursich and Oschmann, 1986; O'Brien, 1986, 1996; Wignall, 1989) have broadly interpreted lithofacies variability in terms of storms, tides and gravity driven currents. The former concentrated on hand specimen scale observations and described these rocks as shale studying the outcrops only. Numerous studies on fine-grained dominated successions deposited on continental shelves have argued that mud-sized material was deposited either in proximal settings in mud belts (e.g. Rine and Ginsburg, 1985) where mud was being transported by wave and tidal processes or in low-energy distal settings as hemipelagites (e.g. Stow and Tabrez, 1998; Hovikoski et al., 2008). This contrasts with slope settings where turbidites (e.g. Stow and Bowen, 1980; Benton and Gray, 1981; Alexander and Morris, 1994; Mulder et al., 1998; Mulder et al., 2001; Pattison, 2005; Cantelli et al., 2008; Lamb et al., 2008), transported by autosuspension processes, are dominant. Notwithstanding the effects of storm set-up on coasts, until recently researchers have argued that ocean currents were not able to move sediments across continental shelves (see for example Swift et al., 1986; Duke et al., 1991; Dalrymple and Cummings, 2005) because of the effect of the Coriollis Force causing geostrophic currents to veer in a shore parallel orientation (e.g. Plint and Walker, 1987). The detection of mudstone in transects, far away from river mouths, across the shelf has drawn much attention about the mechanisms responsible for mud dispersal (e.g. Macquaker, 1994a; Nittrouer and Wright, 1994; Bohacs, 1998; Macquaker et al., 1998; Wright et al., 2001; Friedrichs and Wright, 2004; Macquaker and Bohacs, 2007; Schieber et al., 2007; Traykovski et al., 2007; Hovikoski et al., 2008; Varban and Plint, 2008).

While conventional gravity-driven transport processes (e.g. turbidity currents, hyperpycnal flows) are only effective on slopes >0.7° (e.g. Nittrouer and Wright, 1994; Mulder and Syvitski, 1995; Parsons et al., 2001; Wright et al., 2001; Wright et al., 2002; Friedrichs and Wright, 2004; Wright and Friedrichs, 2006; Hill et al., 2007; Lamb et al., 2008; Lamb and Mohrig, 2009; Macquaker et al., 2010a), however, fewer studies have attempted to elucidate the mechanisms responsible for fine-grained sediments deposition across continental shelf environments that have slopes < 0.5° (e.g. Eel Shelf, Mowry Shale, and Cleveland Ironstone Formation, Yorkshire coast, UK) (e.g. Bentley and Nittrouer, 2003; Macquaker et al., 2010b). Detailed thin section investigations of three samples collected from the above mentioned successions reveal that each sample comprises a stacked succession of thin (<10 mm thick), normally graded beds that have three distinct parts (Figure 1.2). These triplet beds are closely comparable to the textures predicted as being products of Wave Enhanced Sediment Gravity flows of Fluid Mud (a subclass of a sediment gravity flow), which are basically different from the other gravity flows because the turbulent energy required to keep the sediment in suspension is supplied mainly by surface waves and not by the flow itself (e.g. Sternberg et al., 1996; Parsons et al., 2001; Wright and Friedrichs, 2006; Macquaker et al., 2010b). These three part beds are produced because: 1) turbulent-combined-flow traction currents initially transport the sediment leading to the deposition of a homogenous basal laminae-set with weak combined flow ripple laminae, prior to (2) flow conditions evolving to being laminar when turbulence is surpressed and the sediment was being transported as part of a fluid mud flow, before finally (3) suspension settling occurring when the fluid mud freezes and suspension settling occurs. In contrast, within turbidites deposition is dominated by turbulent flow throughout until suspension settling occurs as the flow ceases (see Macquaker et al., 2010) leading to an absence of a triplet fabric.

Tides can generate different bedforms in the continental shelves (see section 2.1). However, most of the classic criteria used for recognizing their deposits (e.g. classic tidal couplets with wave ripple laminae) have not been observed in offshore shelf environments (e.g. Mowry Shale, Cleveland Ironstone Formation and Grey Shale, Cleveland Basin, UK) where tempestites, hummocky cross stratifications and gutter casts are well documented. The presence of these microfabric styles indicate that storms were playing a major role in sediment dispersal within these environments (e.g. Greensmith et al., 1980; Aigner and Reineck, 1982; Macquaker and Taylor, 1996; Rawson and Wright, 1996; Wignall et al., 2005).

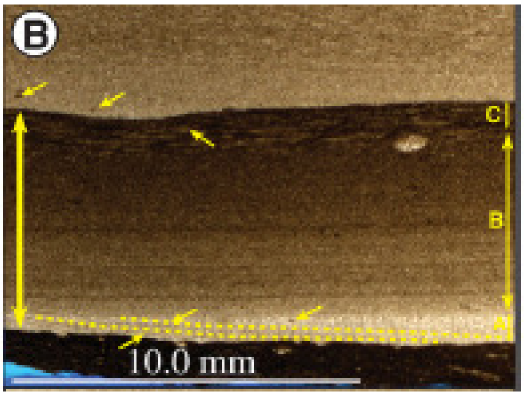

Figure 1.2. Thin section scan of a mudstone collected from the Mowry Shale showing three-part bed motif. The thin bed has an erosional base and is normally graded. Basal lamina sets (unit A) contain silt-sized clay-aggregate intraclasts, and internally may contain curved laminae (dotted lines) that lap down. These basal lamina sets are abruptly overlain by thin intercalated laminae (unit B) composed of clay and silt that subtly grade upward and are capped by burrowed clay drapes (unit C). From Macquaker et al. (2010).

Many studies (e.g. Demaison and Moore, 1980; Savrada and Bottjer, 1987, 1991; Brumsack, 1991; Leithold, 1994; Wignall, 1994) have been conducted using proxy based data to investigate the onshore / offshore variability in mudstones; however, there are very few studies that characterise the microtextural variability in these rocks in order to explain explicitly how the sediment was dispersed around the basin, and what happened to it shortly after it was buried.

Recent high-resolution imaging techniques (e.g. backscattered electron imagery), coupled with more traditional methods (thin section scan and optical petrography) have proved to be very useful in determining the origin of these fine-grained sediments. These techniques reveal that these mudstones exhibit a great deal of previously unrecognised lithofacies variability, particularly at millimetre to 10's of millimetres scales (e.g. Macquaker et al., 1998; Schieber, 1999; Macquaker and Jones, 2002; Macquaker and Adams, 2003). In addition they reveal the microtextural attributes of the sediment and these show that some of the individual thin beds preserve their primary sedimentary structures and / or have been homogenised by burrowing activities. Moreover, they reveal that successive units commonly contain very different proportions of components derived from detrital input, primary production in the basin, and diagenetic processes. The presence of these microtextures is very important as they can give us significant information about the mechanisms that control sediment transportation and dispersal. Crucially, these data indicate that at least episodically the sediment was being transported by advective transport processes; the sea floor was being eroded, and that the bottom waters were not as persistently anoxic and quiescent as many geologists have assumed.

1.4. Aims and objectives of the study

The overall aim of this study is to investigate some of the mechanisms responsible for mud production and subsequent dispersal across continental shelves in the rock record and what happens to this material shortly after deposition and during early diagenesis. In particular, this study aims to: a) investigate the mechanisms responsible for initial production and dispersal and how these might vary in a basin where conditions evolved from an offshore shelf setting to a persistently deep anoxic basin; b) demonstrate that low energy environments and persistent bottom-water “anoxia” are not essential pre-requisites for enhanced organic-matter preservation in ancient mudstones, c) examine if it is practicable to use sequence stratigraphic principle to interpret the facies variability in a mudstone succession that contains both clastic detritus and significant production derived components that have previously been interpreted as being deposited in association with an anoxic event where facies variability is interpreted to be linked to changing primary production and clastic dilution.

In order to meet these aims the following objectives have been identified:

1- Review how mud is dispersed on recent continental shelves, and describe how researchers think mud was being transported on ancient continental shelves.
2- Identify an appropriate study interval to act as a natural laboratory for this study
3- Describe the study area and provide the geological background to this area.
4- Describe the methods used to characterise the sediments in the studied succession so that the fundamental controls on lithofacies variability can be determined.
5- Describe lithofacies present paying particularly attention to their grain sizes, origin

of constituent grains and microtextures present.

6- Describe the temporal distribution of lithofacies.
7- Discuss from where the individual sedimentary components were derived.
8- Discuss likely mechanisms of sediment dispersal across this ancient continental shelf.
9- Discuss the roles of changing accommodation availability and the effects of oxygen concentration.
10- Discuss the effects of sediment colonization and bioturbation.

1.5. Outline of the thesis

The following provides a brief outline of the content of each chapter presented in the thesis. The central chapters (6 to 8) have been written in a format suitable for submission for publication in peer-reviewed journals, and as such, some overlap and repetition of the background information, methodologies, and references is present in order to allow each chapter to be a self-contained ready for publication.

The structure of the thesis is as follows:

- Chapter 1 (Introduction and thesis outline) provides background information about mudstones preserved in ancient continental shelves, why they are so important and what are the main problems regarding their dispersal. It also outlines the key aims and objectives of the study as well as the structure of the thesis.

- Chapters 2 and 3 provide an in-depth literature review of the physical mechanisms that operate on modern and ancient continental shelves to disperse sediments respectively. Chapter 2 includes, specifically, the roles that tides, storms [distal hummocky cross-stratification (HCS), tempestites, gutter casts], density flows [wave-enhanced sediment-gravity flows (WESGFs)], and marine snow play in sediment delivery and dispersal. Chapter 3 includes a general summary of the origin of fine-grained sediments in ancient sedimentary successions. It reviews the overprinting of bioturbation and the effects of bacterially-mediated diagenesis, the use of the term “lamination and bedding”, the role of bottom water anoxia, and the significance of sequence stratigraphy in fine-grained sediments.

- Chapter 4 (Study area and geological background) describes the geological context of the studied succession.

- Chapter 5 (Methodology) describes all the techniques that have been used in this investigation to characterise the studied sediments. This includes descriptions, sampling strategies, preparation of thin sections, analyses of thin sections using optical and electron optical methods and the geochemical techniques.

- Chapter 6 (Manuscript 1), titled "Sediment transport processes in an ancient mud-dominated succession: a comparison of processes operating in marine offshore settings and anoxic basinal environments"). This study describes the lithofacies present in the Cleveland Ironstone Formation and Whitby Mudstone Formation and discusses how physical sedimentological processes might have interacted to control lithofacies variability preserved in this ancient mud-dominated succession, which evolves from a marine offshore settings to a basinal "anoxic" environments.

- Chapter 7 (Manuscript 2), titled "Sedimentological controls on the preservation of organic carbon in fine-grained sediments and the "Goldilocks Condition": a case study of the Grey Shale and Mulgrave Shale (Toarcian, Lower Jurassic) preserved in northeast England") deals with the physical and chemical controls on the preservation of organic matter in fine-grained sediments that contain intervals of both average and elevated organic carbon content.

- Chapter 8 (Manuscript 3), titled "Sequence stratigraphy in organic-carbon rich mudstone successions: a case study of the Whitby Mudstone Formation, NE England" deals with sequence stratigraphy in ancient mud-dominated succession preserved in anoxic basinal environments.

- Finally, in Chapter 9 (Summary) the major findings of the preceding chapters (specifically result Chapters 6 to 8) are summarised into an overarching synthesis. In addition, recommendations for further studies are presented.

- In addition, the appendix, which is presented in an electronic format on a DVD, include: complete results data set (including thin section scan, optical micrograph, electron optical micrograph, and XRD) of all Cleveland Ironstone Formation, Grey Shale Member and Mulgrave Shale Member samples.

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Chapter 2

Mud dispersal on modern continental shelves

Shallow (shelf) seas contain a wide range of facies ranging from conglomerates and sandstones to limestones and mudstones. Facies distributions in these settings are controlled by many factors including: detrital sediment supply, primary production, sediment transport mechanisms, sediment accumulation rates, relative-sea level change, biological mixing and diagenetic transformations. All of these factors are broadly influenced by climate (e.g. see Reading, 1978, 1996; Johnson and Baldwin, 1986; Nichols, 2009). The main processes responsible for sediment dispersal on modern shelves include tides, storms, waves and gravity-driven dispersal mechanisms. These processes, and particularly how they influence mud distributions in this setting, are reviewed in the following sections.

2.1. Tidal processes

A tide is any periodic fluctuation in water level that is generated by the gravitational attraction exerted on oceanic or lake waters by the moon and the sun, with the moon having more than twice the effect of the sun (e.g. Reading, 1978, 1996; Dalrymple, 1992; Nichols, 2009). In most areas the tidal signal is a mix of daily and half-daily tides. In the deep ocean the tidal range is normally a few tens of millimetres but in coastal regions it may be up to many metres (e.g. Bruun, 1962; Dalrymple, 1992; Nichols, 2009).

A tidal current is defined as a periodic horizontal water-flow accompanying the fall and rise of the tide (e.g. Dalrymple, 1992, 2005; Nichols, 2009). The presence of extensive tidal currents is one of the most diagnostic features of many continental shelves. The speed and flow directions of most tidal current vary systematically over a single tidal cycle (e.g. Dalrymple, 1992; Reading, 1996; Nichols, 2009). In open shelf setting, where the direction flow is not restricted by any barriers, the Coriollis force rotates the tidal wave about a fixed (*amphidromic*) point and thus the speed and direction of the tidal current are continuously changing, whereas in nearshore rejoins and because of the shoreline, the current speeds become higher parallel to the coast, and weaker in an onshore-offshore direction (e.g. Swift and Thorne, 1991; Dalrymple, 1992). Tidal currents form a suite of facies and bedforms that are both erosional and depositional (e.g. Belderson and Stride, 1966; Belderson et al., 1982; McCave, 1985; Swift and Thorne, 1991).

Depending on sediment supply, tides generate many bedforms (Figure 2.1), including furrows and gravel waves, sand ribbons, sand waves, sand patches, and finally mud zones typically that are typically located towards the end of tidal current transport paths (e.g. Stride, 1963, 1988; Kenyon, 1970; McCave, 1971; Hamilton and Smith, 1972; Belderson et al., 1982; Johnson and Baldwin, 1986; Dalrymple and Makino, 1989; Dalrymple, 1992, 2005; Miller and Eriksson, 1997). Mud zones are well-developed in regions where both wave activity and tidal current velocity are relatively low (e.g. Stride, 1963; McCave, 1973; Reineck and Singh, 1980; Dalrymple and Makino, 1989; Dalrymple, 1992, 2005; Martin et al., 2008). McCave (1969) suggested that the time available at slack tide is insufficient to let deposition of more than a fraction of a millimetre of sediment and the mechanism, particularly away from the coast, where sediment concentration is low, must be more or less continuous. Although time is insufficient for deposition of fine-grained dispersed sediments at slack water, mud-sized material does accumulate because it is rapidly pelleted and forms flocs. These aggregates, floccules, or pellets behave much like sand or silt grains and can be transported and deposited in various bed-forms (e.g. Macquaker and Bohacs, 2007; Schieber et al., 2007; Schieber and Southard, 2009; Macquaker et al., 2010b). Floccule deposition is influenced by turbulence, bed shear stress, sediment concentration, and settling velocity (e.g. Alldredge and Gotschalk, 1990; Herren et al., 2004; Schieber et al., 2007). McCave (1984a) and Sanford (2008) have concluded that the preservation of fine-grained sediment in the geological record may depend on the consolidation processes of this sediment. They noted that the cohesion of mud containing clay particles makes it more resistant to erosion than the cohesionless sediment, thus such material might be deposited during slack conditions and then remain even if the currents are too strong for normal deposition. In the more distal settings ripples, scour and fill, graded sand and silts interbedded with mud layers, and finally laminated mud which may be interpreted as tidalites are common (e.g. Johnson and Baldwin, 1986; Kuehl et al., 1986; Swift and Thorne, 1991; Miller and Eriksson, 1997; Nichols, 2009).

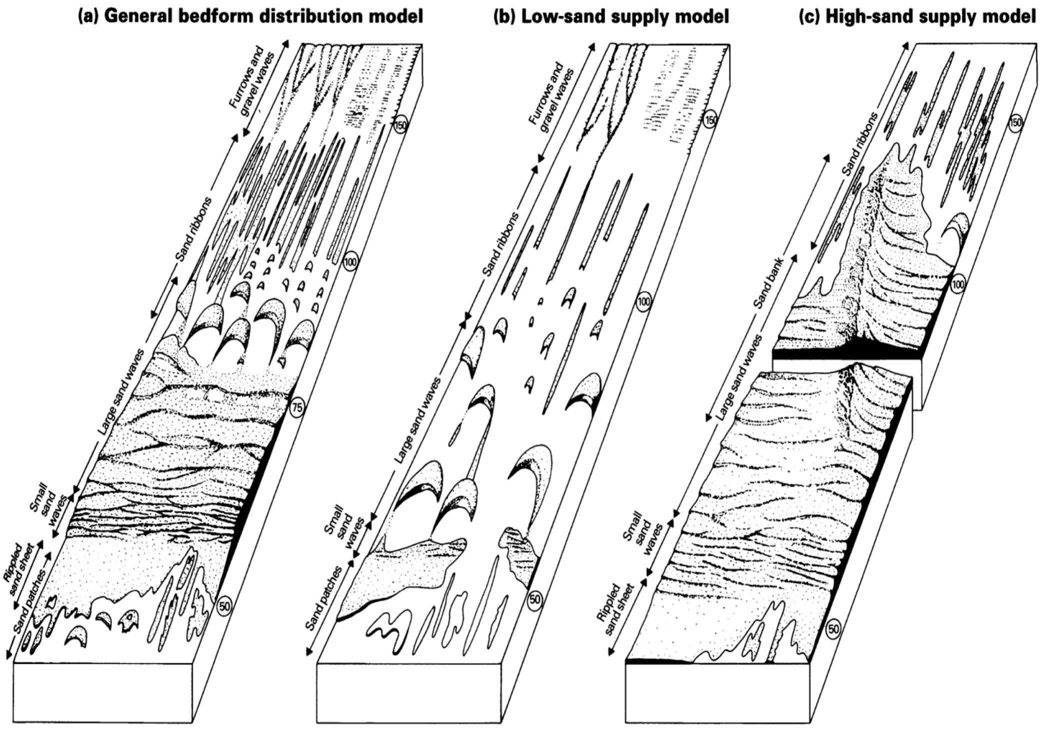


Figure 2.1. Distribution of bedform zones along tidal current transport paths: (a) general model, (b) low sand supply model, and (c) high sand supply model (from Belderson et al., 1982).

2.2. Wave and storm processes

A wave is described as a disturbance travelling through a liquid or solid which involves the transfer of energy between particles (e.g. Zaitlin and Schultz, 1990; Nichols, 2009; Plint, 2010). Storms are created where atmospheric low-pressure centres develop, which are surrounded by high pressure rejoins (e.g. Nichols, 2009; Plint, 2010) and strong winds produced forming waves in the surfaces waters. Wave and storm generated currents are the result of meteorological forces acting on the shallow parts of shelf and oceanic waters (e.g. Ager, 1974; Reading, 1978; Leckie and Walker, 1982; Johnson and Baldwin, 1986; Stride, 1988; Nichols, 2009; Plint, 2010). Large storms can have a significant effect on shallow marine environments, and storm-related processes of sedimentation are dominant in many shelf seas (Nichols, 2009). Waves break and steepen when they meet shallow shelf waters and friction impedes their progress. The wave breaking leads to loss of wave height and energy for a given wave period (e.g. Nittrouer and Wright, 1994). Therefore, the further offshore these conditions are encountered the smaller the waves will be that finally reach the shore. Conversely, deeper waters lying adjacent to coastlines enable waves to travel closer into shore before finally breaking (e.g. Ranasinghe et al., 2004; Slott et al., 2006;

Hemer et al., 2007). Two typical types of water movement are induced as a result of transferred energy through wind shear stress and fluctuation in barometric pressure (Johnson and Baldwin, 1986; Swift and Thorne, 1991): (1) oscillatory and wave-drift currents; and (2) wind-driven currents (Figure 2.2).

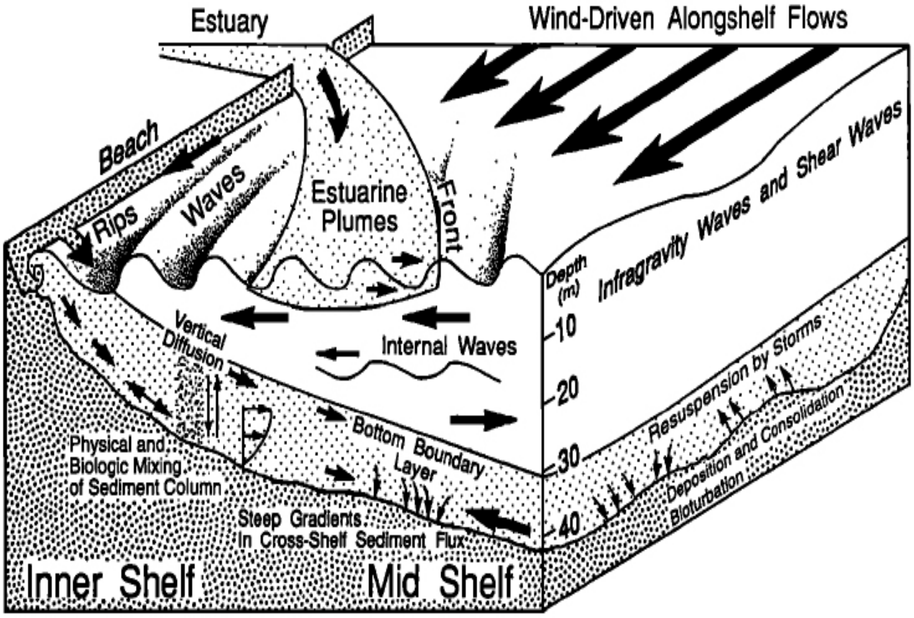


Figure 2.2. The main components of wave-and storm-dominated, inner and mid-shelf dispersal systems (from Nittrouer and Wright, 1994).

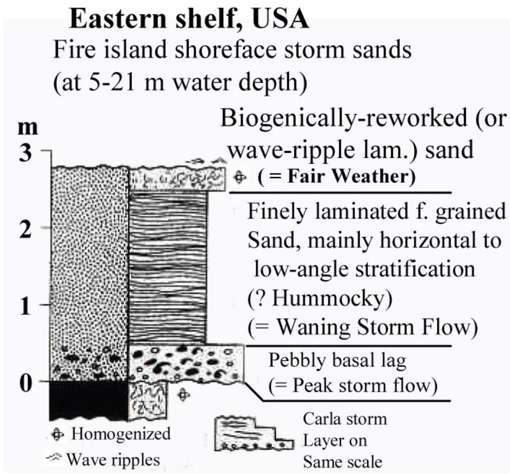
Oscillatory and wave-drift currents are the main components of the storm-fair-weather hydraulic regime, where they interact in dynamic equilibrium to generate a shelf surface specified temporally and spatially by patterns of sediment erosion, transport and deposition (e.g. Johnson and Baldwin, 1986; Swift and Thorne, 1991), whereas wind-driven currents, with energy transferred via turbulent mixing, are the result of wind shear stress on the water surface. They are also considered as the indirect result of atmospheric circulation systems where they operate over a wide range of spatial and temporal scales (e.g. Smith and Hopkins, 1972; Johnson and Baldwin, 1986).

During transportation, fine-grained sediments undergo changes in their effective grain sizes and settling velocities because small grains both form aggregates of variation sizes can be dispersed as individual particles while they are suspended in the water column. This aggregation and dispersal process depends upon turbulence intensities (e.g. McCave, 1984a, 1984b, 2005; McCool and Parsons, 2004; Schieber et al., 2007). McCave (1984a) observed that the fine-grained sediment transport and deposition depends mainly on the settling velocity of the suspended particles which in turn depends on their states of aggregation (see also Eisma, 1986; Alldredge and Silver, 1988; Thornton, 2002; Macquaker et al., 2010b). The term 'suspension' usually refers to material supported by turbulence in a boundary layer (e.g. McCave, 1984a, 2005; Nittrouer et al., 1986; Baas and Best, 2002; Lamb and Parsons, 2005). Numerous authors (e.g. McCave, 1984a, 2005; Rine and Ginsburg, 1985; Nittrouer et al., 1986; Kineke et al., 1996; Wright et al., 1999; Wright et al., 2001; Rotondo and Bentley, 2002; Lamb and Parsons, 2005; Lamb et al., 2008) have studied the influence of waves on the deposition of shallow shelf sediments. They have demonstrated that with appropriate suspended sediment concentrations, deposition of mud may be dampened by wave action. Hourbolt (1968) suggested that the simple existence of a zone of high wave activity does not inhibit deposition of mud when concentrations are high. Under these circumstances, mud can be deposited in areas where both strong tidal currents and high wave activity are impacting the seafloor (see also Rine and Ginsburg, 1985; Rotondo and Bentley, 2003). Kineke et al. (1996) and Rine and Ginsburg (1985) have observed that, in these settings, fluid muds (high-density suspensions with >10g/l suspended sediment concentrations), which occur during decelerating or slack currents where the deposition rate is fast, are not considered part of the consolidated seabed because they lack mechanical strength. In addition, the sediments at the river mouth can experience many cycles of trapping and resuspension before being advectively transported seawards and along shelf, where they are largely incorporated into fluid muds along the bottom salinity front. When formed, these fluid muds can lead to significant wave-supported, gravity-driven, cross-shelf sediment transport (e.g. McCave, 1984a, 2005; Traykovski et al., 2000; Mulder and Alexander, 2001; Wright et al., 2001; Lamb and Parsons, 2005; Macquaker et al., 2010a).

Storms are capable of eroding and then transporting large volumes of sediment on continental shelves. In these settings sediment is transport both as bedload and / or as gravity- / wave-driven fluid mud flows (see below). The patterns and characteristics of storm deposition on modern shelves are controlled by many factors including: nature of the available sediment; energy level of the hydraulic regime; storm-generated current direction; distance from shore-line; water depth; and finally degree of post-storm bio-physical reworking (e.g. Johnson and Baldwin, 1986; Nichols, 2009). Common products of storms in shallow marine environments are tempestites. Tempestites are typical normally graded units that contain marked evidence of aggressive erosion of underlying sediments during the period that the storm was active, followed by rapid re-deposition as the storm wanes (e.g. Ager, 1974; Aigner, 1982; Myrow and Southard, 1996). In proximal settings tempestites typically contain coarse-grained sand and gravel, in contrast to more distal settings where they are usually dominated by silt and mud (e.g. Ager, 1974; Aigner, 1980, 1985; Myrow and Southard, 1996; Einsele, 2000). Tempestites typically contain a fauna that has been transported from its original deposition locus.

Modern storm deposits usually contain the following features (e.g. Hayes, 1967; Kumar and Sanders, 1976; Morton, 1981; Aigner and Reineck, 1982; Reading, 1996; Nichols, 2009): (1) erosion bases; (2) basal lags of mud, shells, and rock fragments; (3) parallel to low-angle lamination, which in three dimensions is hummocky cross-stratification type; (4) wave-ripple lamination; and (5) bioturbated tops (Figure 2.3)

Figure 2.3. General schematic example of modern offshore storm deposits from shelf settings (after Kumar and Sanders, 1976).



In their study on the German Bight (southern North Sea), Aigner and Reineck (1982) revealed that proximal-distal trends show three main associations of storm deposit (Figure 2.4): (1) shoreface sands combined with amalgamated sequences of erosively bounded storm deposits; (2) transition zone of well-preserved storm beds; and (3) shelf mud zone combined with thin and finer-grained storm sand layers.

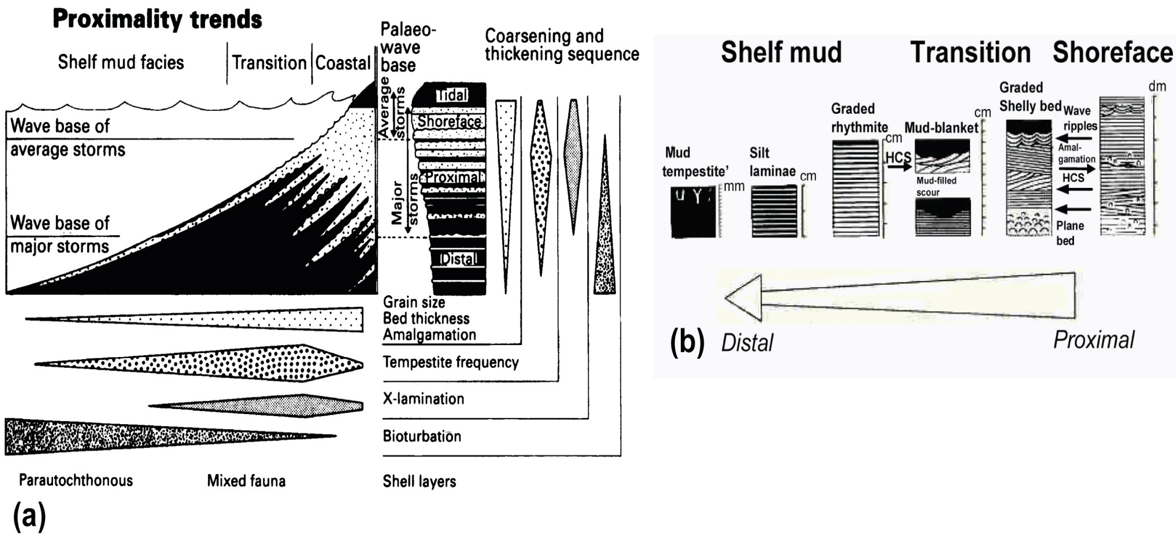


Figure 2.4. Proximal-distal trends in modern shelf storm deposits based on the German Bight: (a) Lateral and vertical variants which define the proximality; (b) lateral variations in individual storm sequences (from Aigner and Reineck, 1982).

Hummocky cross-stratification (HCS) is interpreted as the diagnostic sedimentary structure of an oscillatory current generated by intense storm waves on continental shelves (e.g. Ito, 2001; Mulder et al., 2009). Many authors (including Southard et al., 1990; Wiberg and Harris, 1994; Li and Amos, 1999) have observed, from their measurements on modern shelf floors, that the wavelength of hummocky cross stratification is proportional to the orbital diameters of storm- induced oscillatory flows. According to this relationship, the wavelength could be used as an indicator of the orbital diameters of ancient storm waves as well as the intensity of ancient storms (see Ito, 2001). In storm deposits, two types of structures are also associated with hummocky cross-stratification: (1) wave ripples, wave ripple cross-lamination (Leckie and Walker, 1982); and (2) basal erosional surface, sole marks, primary flow and graded bedding (Mulder et al., 2009) (Figure 2.5).

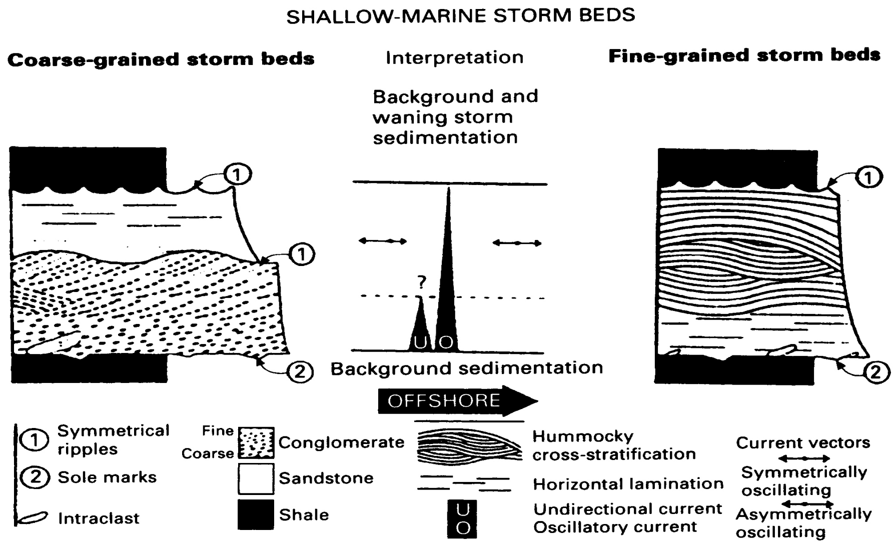


Figure 2.5. Comparison of sedimentary structures in coarse- and fine-grained storm beds (after Cheel and Leckie, 1993).

Gutter casts are elongate downward-bulging, deep and narrow erosional structures of variable sizes produced either by storms under strong offshore-directed unidirectional currents or by geostrophic and wave orbital currents (e.g. Whitaker, 1973; Greensmith et al., 1980; Myrow, 1992; Pearez-Loapez, 2001). They have been described using a variety of terms such as pots, gutters, scour-and-fill, cut-and-fill and furrows (e.g. Greensmith et al., 1980; Aigner, 1985; Myrow, 1992, 1994; Browne, 1994; Myrow and Southard, 1996). These sedimentary structures are of great significance for the interpretation of depositional environments (Pearez-Loapez, 2001). Their size and geometry are likely a function of many variables such as the eroding-flow type and intensity, grain size, diagenetic history, and length of time that erosion takes place (e.g. Myrow, 1992, 1994; Pearez-Loapez, 2001).

2.3. Density flows (wave-enhanced sediment-gravity flows and turbidites)

Traditionally researchers argued that storm-induced turbidity currents were the most important agents of cross shelf transport (e.g. Hamblin and Walker, 1979; Walker, 1985b, 1985a). However, recent field observations from continental shelf environments (Eel Shelf, Louisian Shelf, Papua New Guinea Shelf, Po Delta) have suggested that most currents are not able to move sediment across continental shelves because these currents are more likely to form shore-parallel flows that have been veered by the Coriollis Force (e.g.

Friedrichs and Wright, 2004; Traykovski et al., 2007; Hovikoski et al., 2008; Varban and Plint, 2008a), because in these setting slopes are too low profile to facilitate transport by gravity-driven processes (e.g. Pantin, 1979; Swift, 1985; Nittrouer and Wright, 1994; Hill et al., 2007).

In the geological record, however, scientists commonly observed that mudstone is present widely across much of the shelf in transects far from river mouths (e.g. Nixon, 1973; Macquaker et al., 1998; Bohacs et al., 2005; Hovikoski et al., 2008; Plint et al., 2009; Macquaker et al., 2010a). These new findings have led sedimentologists to reinvestigate the importance of gravity-driven transport processes in dispersing fine-grained sediment across continental shelves (Sternberg et al., 1996; Wright and Friedrichs, 2006; Macquaker et al., 2010a). Wave-enhanced sediment-gravity flows (WESGFs) have been identified as the major mechanism for cross-shelf mud transport (e.g. Wright et al., 2001; Friedrichs and Wright, 2004; Traykovski et al., 2007; Hovikoski et al., 2008; Varban and Plint, 2008b). Such a mechanism requires sufficient sediment supply, and wave-current energy to transport the sediment, even across the low gradient continental shelves (Friedrichs and Wright, 2004; Macquaker et al., 2010a). Wright et al. (2001) and Traykovski et al. (2007) have demonstrated from their investigations on the Eel River and Po River shelves that WESGFs were initiated after a period of river flooding deposited a large volume of sediment on the inner shelf, where that sediment was subsequently subject to resuspension by large waves. In their study, Macquaker et al. (2010a) have related the hydrodynamic conditions to the textures formed before development of a wave-enhanced fluid mud flow (Figure 2.6 Top) and during the flow (Figure 2.6 Bottom). They observed that before development of the flow, wave resuspension (velocity u_w) is extreme and turbulent during the wave boundary layer (at elevation δ_w), sediment [at concentration C (Z)] decreases with elevation above the seabed, and bedforms related with turbulent combined flow form (annotated A in cartoon). As sediment concentrations reach critical values in the wave boundary layer due to the combined effects of advection and resuspension, turbulence in the wave boundary layer is dampened, a pressure gradient develops, and the flow initiates. The earlier bedforms developed under near laminar muddy flow. Shear within the lamina flow leads to the deposition of intercalated silt and clay lamina (annotated B in cartoon) while unit C accumulates during lutocline collapse as flow energy wanes and the flow freezes (Figure 2.6 Bottom).

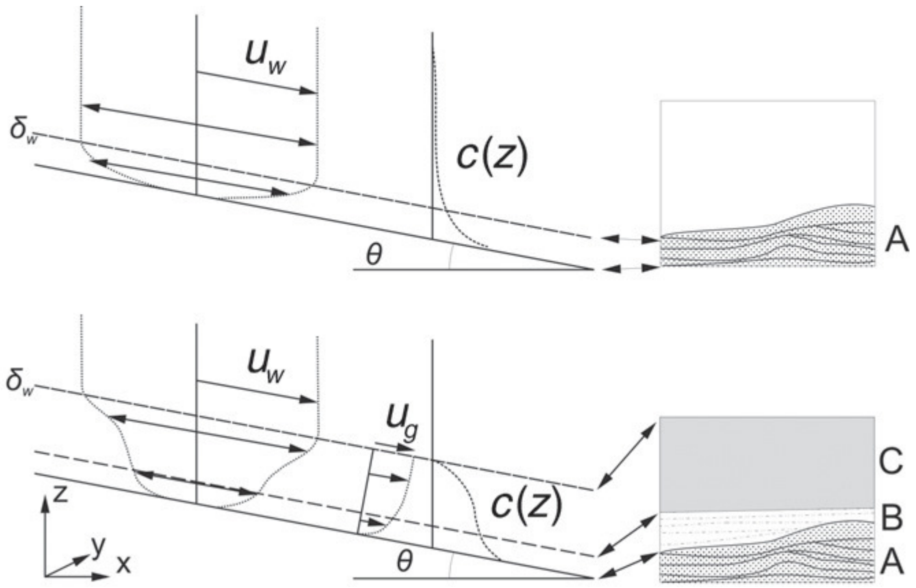


Figure 2.6. Schematic illustration of hydrodynamic conditions and associated bedding before development of WESGF (Top) and during the flow (Bottom). See Macquaker et al. (2010a).

2.4. Marine snow

In the water column, much of the suspended material that ranges in size from a few microns to many centimetres exists as aggregates of organic-derived debris such as micro-organisms, zooplankton fecal pellets, and bacteria, as well as inorganic materials such as clay and silt (e.g. Honjo, 1980; Eisma, 1986; Alldredge and Cohen, 1987; Alldredge and Gotschalk, 1990; Shanks, 2002; Herren et al., 2004; Macquaker et al., 2010b). These organo-minerallic aggregates are ubiquitous and abundant throughout the marine pelagic zone (e.g. Fowler and Knauer, 1986; Alldredge and Silver, 1988; Herren et al., 2004) and described as marine snow, where the particulate aggregates are larger than 0.5 mm in diameter, and phytodetritus where they are smaller than 0.5 mm (e.g. Suzuki and Kato, 1953; Alldredge and Silver, 1988). They are held together in the water column by the presence of extracellular muco-polysaccharides, secreted by marine plankton and acting as "glue" when the particles come into contact with one-another (e.g. McCave, 1984b; Eisma, 1986; Nittrouer et al., 1986; Nittrouer and DeMaster, 1986; Alldredge and Silver, 1988; Alldredge and Gotschalk, 1990; Thornton, 2002).

Many researchers (e.g. Alldredge, 1976; Billett et al., 1983; Kranck, 1984; Lampitt, 1985; Thiel, 1995; Fortier et al., 2002) have noted from their studies on modern oceans that marine snow is mostly associated with phytoplankton blooms and settles rapidly as they have settling rates orders of magnitude greater than individual grains (i.e. up to 2100m/day for large zooplankton fecal pellets (e.g. Thiel, 1995)).

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Chapter 3

Background to the study

In the second chapter the sediment transport processes occurring on recent shelf seas and their bedform products were discussed. However, the fundamental mechanisms (physical, chemical and biological) that contribute to the origin of fine- grained sediments in ancient shelf seas are not well-studied. The main purpose of this section is to review previous studies of fine-grained sediments, specifically: (1) how they were formed, and (2) the processes that modified them during early burial. In addition the terms used to describe the stratigraphic building blocks of mudstones (e.g. lamination, bedding, parasequences and systems tracts) and the intervening surfaces are defined.

3.1. Sources of fine-grained sediments in ancient sedimentary successions

Like most sedimentary rocks, fine-grained sediments contain materials from three sources; clastic (allochthonous or detrital-derived components), biogenic (autochthonous or production-derived components), and diagenesis-derived components (e.g. Potter et al., 1980; Chamley, 1989; Macquaker and Gawthorpe, 1993; Macquaker et al., 2007; Nichols, 2009).

Clastic components are mostly produced at the earth's surface and rivers by erosion (physical abrasion by ice, river bedload and by aeolian transport in deserts) in addition to chemical weathering of pre-existing muds, mudstones, and igneous and metamorphic rocks in soils (e.g. Potter et al., 1980; Chamley, 1989; Potter et al., 2005). Organisms that pulverize and ingest sediment are minor sources of terrigenous mud (e.g. Chamley, 1989). Other sources include volcanic dust (perhaps a major source during early Earth history).

Biogenic components (e.g. foraminifers, amorphous organic matter, coccoliths, diatoms, radiolaria, and algae) are the organisms that live within the water column as well as in the surface sediment layers and contribute much of the autochthonous component in areas of high primary production. Many authors (including Pedersen and Calvert, 1990; Tyson, 1995, 2005a; Bohacs et al., 2000; Bohacs et al., 2005; Katz, 2005) have noted that the primary productivity is controlled, in large part, by the availability of nutrients (including $H_2PO_4^-$, NO_3^- H_4SiO_4, and dissolved Fe). Cook and McElhinney (1979) and Hay (1995) mentioned that the nutrient supply from rivers may be restricted because of estuarine trapping. When nutrients escape the estuary, they are often combined with terrestrial organic matter and thereby reduce the oil-proneness of the sediment, while increasing its gas-prone tendencies. Tribovillard et al. (1996) and Tribovillard et al. (2005) argued that the nature of the primary productivity itself may play a role in whether organic matter accumulates. They suggested that less organic matter accumulates in systems dominated by cocolithophorids than where primary productivity is dominated by diatoms or plankton without skeletal tests. The type of organic matter and the amount of its supply could also play an important role in its accumulation. Numerous authors (e.g. Hedges and Keil, 1995; Tyson, 1995, 2005a; Hedges et al., 1999; Katz, 2005) have suggested that plankton-derived organic matter degrades more quickly under oxic conditions than organic matter derived from vascular plants as a result of their chemical differences (carbohydrates and nitrogenous compounds versus lignin).

Diagenetic-derived components are the materials that precipitate either at the sediment-water interface (seabed), or once the sediment is buried (e.g. Potter et al., 2005; Macquaker et al., 2007; Nichols, 2009). They commonly include aragonite.

3.2. Bioturbation (early oxic diagenesis) and compaction

Once the various components of fine-grained sediments are produced, it is likely that they were mostly transported by mechanisms such as tides, waves, and storms from their sources to their depositional basins. Once deposited, their original fabric can be disrupted by different secondary mechanisms such as bioturbation and compaction.

Bioturbation is defined as sediment mixing by organisms. The effects of bioturbation on the fabric of fine-grained sediments has been discussed by many authors (e.g. Droser and Bottjer, 1986; O'Brien, 1986; Savrada and Bottjer, 1987, 1989; Schieber, 1990, 1999, 2003; Wignall and Hallam, 1991; Bromley, 1996; Stow and Tabrez, 1998; Pemberton et al., 2001; Bentley and Sheremet, 2003; Bentley et al., 2006; McIlroy, 2007; Tonkin et al., 2010). Analyses of the fabrics produced by burrowing organisms, in addition to the fabrics produced while the sediment was being deposited, are important for understanding the conditions under which the silt and clay-sized components were sedimented (see O'Brien, 1986; Francus, 2001). In fine-grained sediment, bioturbation can be classified in terms of factors such as sediment packing, sediment mixing, sediment cleaning, as well as pipe-work building strategies (e.g. Bentley and Sheremet, 2003; Tonkin et al., 2010). In continental shelves, bioturbation style and intensity are controlled by the availability of reductants (food) and oxidants (oxygen by diffusion) as well as the presence of H_2S and the recurrence frequency of sediment delivery events (e.g. Macquaker and Howell, 1999; Bentley and Sheremet, 2003; Bentley et al., 2006; Macquaker et al., 2007; Macquaker et al., 2010). Bioturbation can furnish information about presence or absence of oxygen in the water column. Burrowing disrupts the primary fabric and reveals wide variations in macro and microfabrics attributed to the degree of bioturbation (see Droser and Bottjer, 1986; Schieber, 2003).

Many workers attributed the preferred grain orientation, particular of the clay fraction, that defines the “shale” fabric, to the mechanical rearrangement of sediment particles during overburden-induced compaction of clay (see for example Curtis et al., 1980; Bennett et al., 1981; Lash and Blood, 2004). This fabric is particularly obvious when mudstones weather and generate fissility. This compaction fabric is also evident where pyrite framboids are present (e.g. O'Brien, 1995).

3.3. Bottom water anoxia

Anoxic conditions occur when oxygen consumption exceeds supply. Anoxia can exist in the water column and is commonly present in the sediment pore waters. Oxygen is supplied to the upper part of the water column by diffusion and mixing at the air-sea interface and to the deeper level through the formation of bottom waters (e.g. Demaison and Moore, 1980; Arthur et al., 1987; Tyson and Pearson, 1991; Arthur and Sageman, 1994; Tyson, 1995, 1996; Paerl et al., 1998; Pearce et al., 2008). Tyson and Pearson (1991) and Tyson (2005b) noted that circulation patterns are the main factors controlling bottom water formation and the likelihood of the bottom waters becoming anoxic. Historically, the condition of persistent bottom water anoxia are commonly invoked as being essential for the preservation of organic carbon-rich sediment and commonly these periods are linked to extinction events (e.g. Demaison and Moore, 1980; Arthur and Sageman, 1994; Wignall, 1994a; Tyson, 1995; Wilkin et al., 1996; Arthur and Dean, 1998; Sinninghe Damaste et al., 1998; Stow et al., 2001; Kenig et al., 2004; Katz, 2005; Van Dongen et al., 2006; Wignall and Bond, 2008). Tyson (1996) proposed that the presence of bottom-water and pore-water anoxia impacts upon organic matter preservation. He listed three ways, each having in common the rapid transfer of organic matter with minimum exposure to oxygen into an anoxic environment: (1) increasing the supply of organic matter (see also Paerl et al., 1998); (2) increasing the rates of sediment deposition; (3) reducing resupply of oxygen to levels near or below the oxygen demand. Demaison and Moore (1980) suggested that the absence of benthic scavengers under anoxic conditions enhances organic preservation by reducing the direct consumption of organic matter through the lack of ingestion and the passage of organic matter through the guts of organisms.

Although persistent bottom water anoxia has been proposed by many authors as being pre-requisite for organic carbon preservation, recent petrographic studies on organic carbon-rich mudstones, however, show that some aspects of this model need to be modified (see for example Macquaker and Gawthorpe, 1993; Macquaker et al., 1998; Macquaker et al., 2010). Their data indicate that long-term persistent anoxia is unlikely to have existed even if the sediment preserves high quantities of organic matter. Instead, their observations suggest that the high concentration of preserved organic matter was linked to the occurrence of episodic phytoplankton blooms where anoxia may have been developed during these events and that between blooms events there was commonly sufficient time and oxygen available for organisms to colonize the sediment. Anoxia was therefore a by-product of organic carbon preservation not a pre-requisite for organic carbon preservation.

3.4. Effects of early diagenesis

Fewer diagenetic studies have been conducted on ancient, fine-grained sediments compared to their coarser-grained counterparts (e.g. Berner, 1970; Irwin et al., 1977; Froelich et al., 1979; Raiswell and Berner, 1985; Raiswell, 1988; Canfield, 1989b; Raiswell and Al-Biatty, 1989; Canfield and Raiswell, 1991; Macquaker, 1994; Coleman and Raiswell, 1995; Curtis, 1995; Taylor and Curtis, 1995; Macquaker et al., 1997; Taylor and Macquaker, 2000a, 2000b; Rickard and Luther, 2007). Many of these studies have observed that bacterially-mediated reactions (e.g., sulfate reduction, iron and manganese oxide reduction as well as methane oogenesis) are important mechanisms controlling the diagenetic process that occur during early burial (e.g. Canfield, 1989b, 1989a; Canfield et al., 1993; Macquaker et al., 1997; Taylor, 1998). Rickard and Luther (2007), noted that sulfate reduction was particularly significant because dissolved sulfate is the most abundant oxidant present in seawater.

Once mud has been buried to a depth of a few tens of meters all the reactive iron will have been reduced (because of the reactivity of Fe(III) in early diagenetic environments) and will not be available deeper (> 1.0 km) to participate in later diagenetic processes (Macquaker et al., 1997). Many authors (including Berner, 1970, 1984; Raiswell, 1982, 1993) have considered early diagenetic reactions which involve iron and have demonstrated links between degree of pyritization (DOP) and iron availability at the time of early diagenesis. Pyrite (FeS_2) is a common mineral produced during early diagenesis in organic-rich sediments. It results from the reaction of sulfide with either Fe (III) or Fe (II) in sediments (e.g. Berner, 1970; Lovley, 1991). Pyrite framboids have been cited as a key to understanding water-column chemistry in ancient strata (e.g. Wilkin et al., 1996; Wilkin et al., 1997; Bond et al., 2004). The nature and style of pyrite formation is commonly dependent on whether porewaters are dominated by either Fe^{2+} or sulfide (e.g. Canfield and Raiswell, 1991; Rickard, 1997). In marine sediments, during earliest diagenesis porewater sulfide is typically buffered to low levels by the presence of highly reactive iron oxides, resulting in iron-dominated porewaters (dissolved iron concentrations > dissolved sulfide). Depending on the rate of sulfide production, pyrite will form either at or away from sites of sulfide production. After consumption of reactive iron oxides, sulfide builds up in porewaters commonly leading to a deeper zone of sulfide-dominated porewaters (see Canfield and Raiswell, 1991; Taylor and Macquaker, 2000b).

The diagenetic evolution of mudstones has been discussed by many authors (e.g. Raiswell, 1988; Curtis, 1995; Arzani, 1997; Macquaker et al., 1997; Taylor and Macquaker, 2000b; Albani et al., 2002). Pre-compaction carbonate cementation in the argillaceous sediments is considered as one of the most important diagenetic modifications during the burial history of ancient mudstones (Raiswell, 1988; Curtis, 1995). The early Jurassic, lower Lias of SW Britain, for instance, comprise alternations of limestones- marls and organic-rich mudstones and typify epeiric sea, offshore sediments that altered chiefly by diagenesis (see Weedon, 1986; Arzani, 1997). All the investigations showed that the laminated limestones, which were developed between the organic-rich mudstone, were formed by the cementation of the pre-compaction mud, prior to organic-rich mudstone formation (Weedon, 1986; Arzani, 1997, 2004). Also they revealed that the diagenetic processes lead to adjustment in clay and organic- rich sediments to form very important authigenic mineral accumulations, among which carbonate cementation is an important process to form limestone nodules that laterally spread within the beds (e.g. Gluyas, 1983; Cuomo and Bartholomew, 1991; Curtis, 1995; Arzani, 2004). Moreover, carbon and oxygen isotopic analyses combined with higher resolution petrographic investigations (backscattered electron microscopy, SEM) showed that the limestones have been formed through the cementation of their enclosed organic rich muds (e.g. Bjorlykke, 1973; Gautier, 1982; Gluyas, 1983; Curtis, 1995; Arzani, 1997, 2004; Raiswell and Fisher, 2000).

3.5. Fine-grained sediment lamination and bedding

Most studies on fine-grained sedimentary rocks have used either field or hand-specimen scale observations or measured proxies to produce descriptions (such as black shale, oil shale) to characterise these sediments (e.g. Oertel and Curtis, 1972; Potter et al., 1980; Weaver, 1989). Their descriptions, however, raised much terminological confusion about the usage of the terms “lamination” and “bedding” in successions that comprise interbedded layers of “muddy sandstones”, “organic-rich mudstones”, and “shale”. Here, problems are caused because the terms used refer both to the vertical distance between partings and the origin of the individual units. For example, Lundegard and Samuels (1980) defined lamination in mudstones as being the parallel arrangement of layers < 10 mm thick that result from the regular alternation in fabric, grain size, and/or colour while they defined beds as layers ranging in thickness from centimetres to tens of meters. Laminae are also defined as being the smallest megascopic layers in a sedimentary sequence. They are bounded above and below by surfaces named lamina surfaces. They are characterized by smaller areal extents and are likely formed over shorter time intervals because they are contained within beds (see Campbell, 1967; Van Wagoner et al., 1990). Beds are commonly layers of sedimentary rock separated by surfaces called bedding planes. Campbell (1967) defined bedding surfaces as depositional surfaces that reveal the principal rock layering or bedding. They are used to subdivide successions of sedimentary rock into their beds and are traditionally used to determine the relative order and timing of the accumulation of the sediments forming the beds. In mudstone successions individual thin-beds are commonly less than 10 mm thick, with sharp / scoured bases (Figure 3.1, A-B). They are the product of depositional events that are separated from one and another by periods of non-deposition (e.g. Macquaker and Gawthorpe, 1993; Macquaker and Taylor, 1996; Macquaker and Howell, 1999).

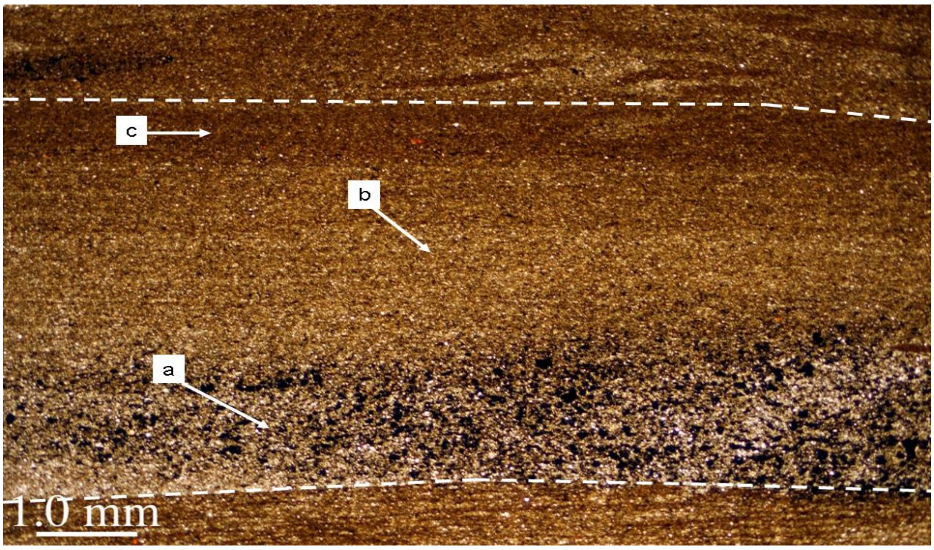

Figure 3.1. (A) Thin section photomicrograph showing individual genetic bed (Macquaker, 2007); (a) homogeneous silt rich; (b) continuous laminae (composed of thin layers of silt intercalated with thin layers of clay); (c) clay rich and the upper part is bioturbated.

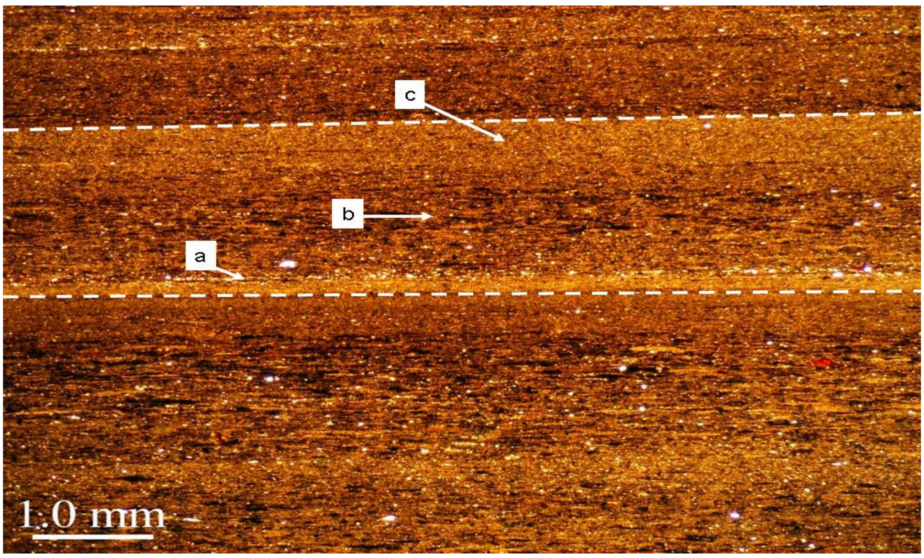

Figure 3.1. (B) Thin section photomicrograph showing three thin beds in mudstones (Macquaker, 2007). Each bed comprises: (a) silt rich laminae at their base, (b) organo-minerallic aggregates in their centres, and (c) bioturbation at their tops.

3.6. Fine-grained sediments and sequence stratigraphy

Sequence stratigraphic principles i.e. dividing the succession into genetically related packages separated by chronostratigraphic surfaces (e.g. Van Wagoner et al., 1990) have not been commonly applied to fine grained successions because at hand-specimen and greater scales these rocks appear homogeneous and rarely exhibit any obvious sedimentary fabrics. This has meant that they have been most commonly interpreted in terms varying primary production, clastic dilution and bottom water anoxia (e.g. Savrada and Bottjer, 1987, 1991; Wignall, 1994a, 1994b; Tyson, 2001) that are overall under the control of climate change. Nonetheless, a few mud-dominated successions (e.g. the Cleveland Ironstone Formation, Mancos Shale, Lower Devonian shales) have been interpreted using sequence stratigraphic methods (e.g. Bohacs and Schwalbach, 1992; Macquaker and Taylor, 1996; Macquaker et al., 1998; Macquaker and Howell, 1999; Schieber, 1999; Macquaker and Jones, 2002; Macquaker et al., 2007), because the authors have been able to identify systematic grain size variability using sieving methods (e.g. Leithold, 1994; Sethi and Leithold, 1994), petro-physical (e.g. Creanney and Passey, 1993) and petrographic methods (e.g. Macquaker and Taylor, 1996; Schieber, 1999).

In spite of appearing relatively similar at hand-specimen scales, recently researchers have been able to identify laminae, beds and parasequences, stratal surfaces and systems tracts in mudstone dominated successions (e.g. Cleveland Ironstone Formation, Kimmeridge Clay Formation, and Oxford Clay Formation). These studies have revealed that the mudstone units were found to be heterogeneous on both small-scale (dm to m) and large-scale (1 m to 5 m). Particularly, these stacked successions of thin beds are organised into small scale (0.1 – 1.0 m) upward-coarsening units and larger scale (1.0 – 5.0m) upward-coarsening and upward-fining units that are capped by units that commonly contain significant diagenetic components (see Macquaker and Taylor, 1996; Macquaker et al., 1999; Macquaker and Howell, 1999; Taylor and Macquaker, 2000a; Macquaker and Jones, 2002). Using sequence stratigraphic principles, the small-scale upward-coarsening units were interpreted to be parasequences, and the large-scale upward-coarsening and upward-fining successions were considered to be high stand system tracts and transgressive system tracts respectively. The analyses also revealed that the cemented beds between the transgressive system tracts and the larger scale coarsening-upward successions are candidates for stratal surfaces whose origins are linked to breaks in sediment accumulation (see Macquaker et al., 1998).

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Chapter 4

Study area and geological background

4.1. Study area

In order to address how the mudstone lithofacies vary in a succession that gradually deepens from an offshore transition environment throughout to a deep anoxic basinal environment, the Lower Jurassic succession from the Cleveland Ironstone Formation through to the Mulgrave Shale Member (Jet Rock) in the Cleveland Basin, North Yorkshire Coast, England was chosen as a 'natural laboratory' to investigate how these processes evolve. In this section the geological context of the studied succession will be reviewed.

In North Yorkshire these Jurassic strata (Figure 4.1), are well-exposed in several locations along the coast, (e.g. Staithes: NZ 78017 18140, Port Mulgrave: NZ 79463 17395, and Runswick Bay: NZ 80662 16138). The section between Staithes and Port Mulgrave were specifically chosen for this study. These strata include the Cleveland Ironstone and Whitby Mudstone Formations (Grey Shale Member and Mulgrave Shale Member respectively) and are predominantly composed of mudstones and muddy sandstones, with minor ironstones and concretionary carbonates. (e.g. Baker, 1863; Hemingway and Knox, 1973; Rawson et al., 1983; Powell, 1984, 2010; Rawson and Wright, 1992, 1996, 2000; Sælen et al., 1995; Macquaker and Taylor, 1996; Taylor and Macquaker, 2000; Wignall et al., 2005).

4.2. Geological background

Located near the western margin of an extensive lowland, the Yorkshire coast area was transgressed by a shallow sea during the late Triassic (Rawson and Wright, 1996). At about the same time regional extension developed across eastern England which led to the development of the Cleveland Basin over North Yorkshire (e.g. Rawson and Wright, 1996; Powell, 2010). During the Jurassic, the Cleveland Basin was relatively small and formed part of small extensional tectonic basins, connected to the North Sea Basin via the Sole Pit Basin in the East (Ziegler, 1982; Powell, 2010). The basin was aerially bounded by the Pennine High to the west, by the Mid-North Sea High to the northeast, and by the Market Weighton High (MWH) to the south (Rawson and Wright, 1996; Powell, 2010) (Figure 4.2). Regionally, most of the bounding faults that affected the Cleveland Basin were active while sedimentation was occurring during Early and Mid Jurassic times (Figure 4.3) (e.g. Hemingway, 1974; Kirby and Swallow, 1987; Milsom and Rawson, 1989; Powell, 1992). For instance, on the southern margin the Howardian-Flamborough Fault Belt was sporadically active north of the Market Weighton High (e.g. Kirby and Swallow, 1987; Wright, 2009). To the east, the basin is defined by Peak Trough and Peak Fault, Cayton Bay Fault, and Whitby Fault (Milsom and Rawson, 1989; Powell, 2010). The northern margin of the present-day outcrop is defined by Redcar Fault zone while the western margin is marked by the north-trending Borrowby Graben (Powell, 1992, 2010).

Figure 4.1. Simplified geological map of the Jurassic strata of the Cleveland Basin, illustrating the main localities and location of deep boreholes, from Powell (2010) after Hemingway (1974) with additions from British Geological Survey (1998); British Geological Survey (2000).

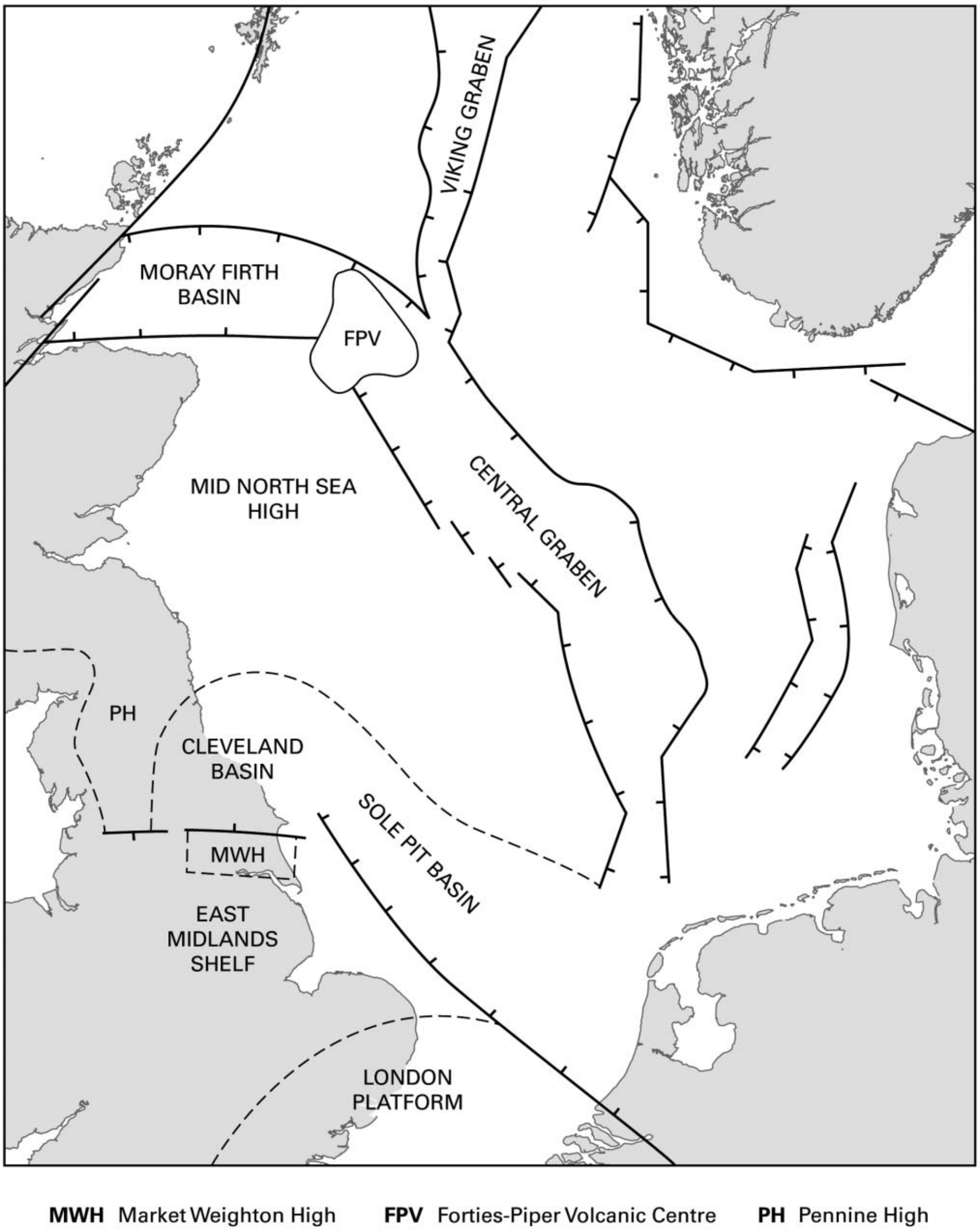

Figure 4.2. Generalized palaeogeographical setting of the Cleveland Basin during the Jurassic, from Powell (2010) after Knox et al. (1991).

The region experienced uplift and erosion during the Middle Jurassic. This uplift was in response to doming and tilting that was occurring in the central North Sea Basin to the east (e.g. Sellwood and Hallam, 1974; Ziegler, 1982; Underhill and Partington, 1993). In the Cleveland Basin, the sedimentation of the Middle Jurassic was therefore characterized by deltaic and fluvial siliciclastic progradation towards the south-east, and by marine transgressions, as the result of occasional sea-level rise, advanced generally towards the north-west over the Market Weighton High (Hemingway, 1974; Powell, 2010) (Figure

4.2). During the early Callovian, rapid sea-level rise throughout Britain resulted in widespread marine sedimentation and partial drowning of the Cleveland Basin over northern Britain (e.g. Powell, 1992, 2010).

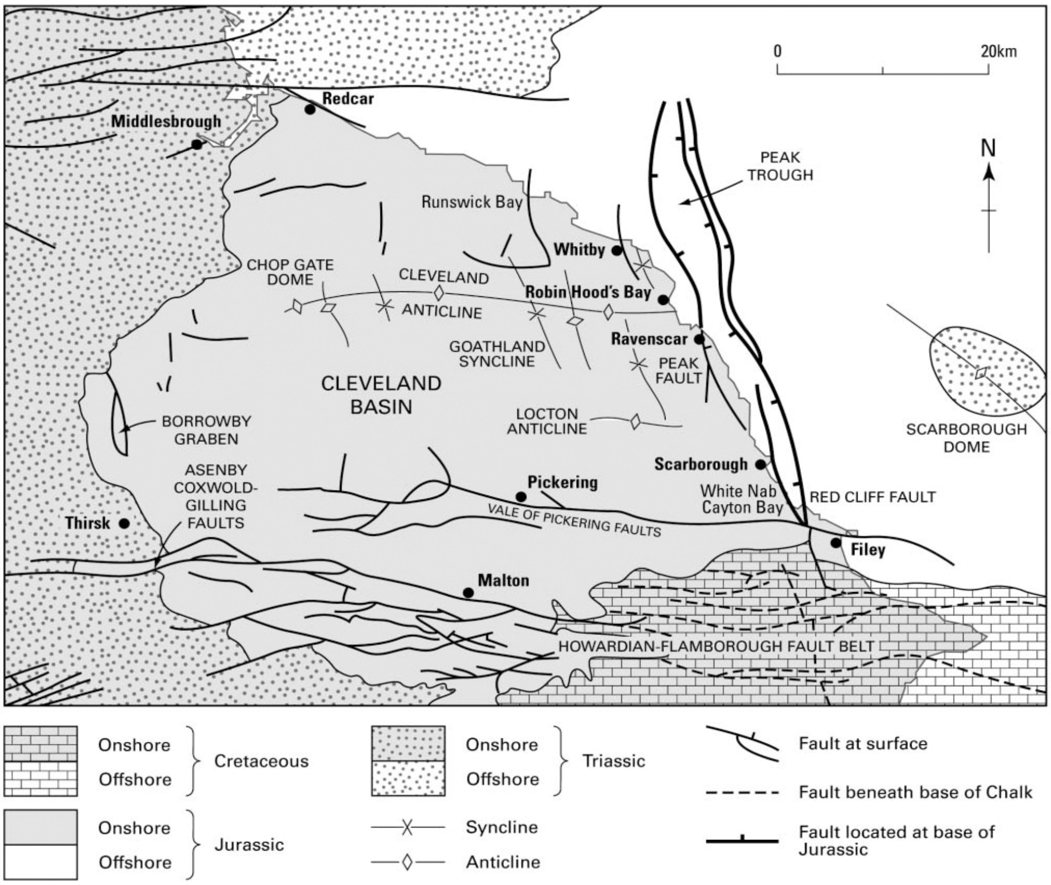

Figure 4.3. Major structural setting of the Cleveland Basin. From Powell (2010) after Kirby and Swallow (1987), Milsom and Rawson (1989), and Rawson and Wright (1996).

During the Early Jurassic marine sediments started to accumulate in the deepening Cleveland Basin. Initially in the Hettangian to Sinemurian a thick pile (up to 313 m thick) of predominantly siliciclastic mudstones (the Lias Group) was deposited (e.g. Rawson and Wright, 1996; Powell, 2010). This was followed by deposition of the 25 m thick Cleveland Ironstone Formation in the Pliensbachian. The Cleveland Ironstone Formation is subdivided into the Lower Penny Nab Member (Howard, 1985), which includes four main iron-seams (Osmotherly, Avicula, Raisdale, and Two Foot seams), and the overlying Kettleness Member, which includes the Pecten and Main seams (e.g. Howarth, 1973; Rawson et al., 1983; Powell, 1984, 1992, 2010; Howard, 1985). The Cleveland Ironstone Formation is characterized by very fine-grained muddy sandstone, coarser-grained siliciclastic mudstones, some calcareous concretionary units, and sideritic and berthierine-rich ooidal facies that capped overall coarsening-upward successions with fossils that include: Bivalves, Brachiopods, Belemnite, and Ammonites (e.g. Hemingway, 1974; Rawson et al., 1983; Howard, 1985; Macquaker and Taylor, 1996; Rawson and Wright, 1996). A variety of fabrics such as gutter casts, distal tempestites, wave ripple laminae, and graded laminae have been observed in this formation. The presence of these fossils and sedimentary structures have led geologists to conclude that this formation was deposited in a normal marine, shallow shelf sporadically swept by storms (e.g. Greensmith et al., 1980; Rawson et al., 1983; Rawson and Wright, 1996).

The overlying Whitby Mudstone Formation (Upper Lias, c. 22m thick) consists predominantly of grey to dark grey mudstones and siltstones with abundant shelly fossils in some intervals (e.g. Powell, 1984, 2010; Milsom and Rawson, 1989). Its lower unit, the Grey Shale Member which is approximately 13m thick, consists of non-fissile, and pale to medium grey silty shales with bands of calcareous and sideritic nodules (e.g. Howarth, 1962, 1973; Powell, 1984, 2010; Wignall and Hallam, 1991; Sælen et al., 1995; Sælen et al., 2000; Wignall et al., 2005). This unit was likely deposited on a marine shelf where the bottom waters varied from fully oxic to dysoxic. The overlying Mulgrave Shale Member (also known as the Jet Rock) comprises 8 m of fissile, compacted and laminated, organic-carbon-rich mudstones with abundant pyrite and rare shell pavements composed of Ammonite and Belemnite fossils with concretionary carbonates (e.g. Pye and Krinsley, 1986; Myers and Wignall, 1987; Rawson and Wright, 1996; Kemp et al., 2005; Wignall et al., 2005). Isotopic data collected from this interval showed that the $\delta^{13}C_{carbon}$ values of the calcite cement range from –12.9 to – 15.4%, the $\delta^{13}C_{organic}$ range from – 26.1 to – 37.0%, the sulphur isotope ($\delta^{34}S$) values of the pyrite range from –22 to – 26%, while the $\delta^{18}O$ values of the calcite range from – 8.9 to – 9.9% (e.g. Raiswell, 1976, 1982; Coleman and Raiswell, 1981; Kemp et al., 2005; McArthur et al., 2008a; Caswell et al., 2009). This unit is interpreted to have been deposited in "anoxic bottom conditions" and coincides with one of the most severe mass extinction events recorded in the Mesozoic Era (e.g. Pye and Krinsley, 1986; Sælen et al., 2000; Wignall et al., 2005; McArthur et al., 2008a; McArthur et al., 2008b; Wignall and Bond, 2008; Caswell et al., 2009; Powell, 2010). In association with more rapid deepening, the Whitby Mudstone Formation was deposited by the effects of low energy suspension settling associated with increasing development of persistent anoxia under fully marine conditions below and close to storm wave-base (e.g. Jenkyns, 1988; Sælen et al., 1996; Jenkyns and Clayton, 1997; Wignall et al., 2005; Powell, 2010).

The overlying Alum Shale member comprises 37 m of less fossiliferous, grey silty mudstone associated with bands of sideritic and calcareous concretions as well as bands of phosphatic nodules in the upper part (Knox, 1984; Powell, 1984, 2010). This unit was likely deposited under more oxygenated marine shelf conditions (e.g. Hemingway, 1974; Powell, 2010). The regional Mid-Cimmerian Dogger Formation overlies unconformably on this unit over much of the Cleveland Basin (e.g. Powell, 1984, 2010), and was produced in response to domal uplift associated with the presence of volcanic activity in the Mid-North Sea region (Underhill and Partington, 1993). This unconformity, defines the end of Lower Jurassic deposition in the Cleveland Basin.

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Chapter 5

Methodology

5.1. Introduction

To investigate the fundamental controls on lithofacies variability and organic-matter preservation in the Lower Jurassic; Cleveland Ironstone Formation, Grey Shale Member, and Mulgrave Shale Member (Cleveland Basin, North Yorkshire Coast, England), it was necessary to identify the constituent rock components and identify the fabrics present in the individual units that make up this succession. With these data the key physical, chemical and biological processes that were responsible for forming these sediments can be identified and the fundamental stratigraphic building blocks namely: laminae, beds, parasequences, and systems tracts, as well as their bounding surfaces namely: bedding planes, parasequences, and the key stratal surfaces (e.g. maximum flooding surfaces, sequence boundaries and transgressive surfaces) can be determined.

In this chapter, all the investigative methods and the rationale for employing them during this study are described. These include the: field work procedures and sampling strategies, as well as the petrographic, analytical and geochemical techniques. A brief description of the rock nomenclature scheme is also included at the end of this chapter. Detailed sedimentological observations of the outcrop combined with well-constrained sampling strategies were required to obtain the necessary samples to generate the key high-resolution descriptions of these fine-grained sediments. Once the samples had been obtained high-resolution descriptions were generated using conventional petrographic, analytical and geochemical methods (obtained variously from both optical, and scanning electron-optical microscopy, X-ray diffraction (XRD), and total organic carbon (TOC) techniques). These data allowed semi-quantitative estimates of the components of individual samples and the proportion of different minerals to be generated (e.g. Macquaker and Gawthorpe, 1993; Macquaker, 1994b, a; Macquaker et al., 1998; Macquaker and Howell, 1999; Macquaker and Adams, 2003; Macquaker and Keller, 2005; Macquaker et al., 2007). Moreover, this approach allowed the primary and diagenetic features within these fine-grained sediments to be distinguished thereby minimizing the effects of component misidentification that is inherent in proxy methods that rely on low resolution data from exposure and core; for example interpreting fissile shales to being laminated rather than thin bedded and misascribing the coccolith component to being a diagenetic component of the rock.

5.2. Field work procedures

To determine the large scale stacking patterns (10^{-1} to 10^{1} m) present within the targeted part of the Lower Jurassic aged sediments in the Cleveland Basin, three different outcrop sections were selected for detailed study. Sedimentary logging measured at the scale of 1:50 and samples were obtained every 0.25 m along a 4 km-long transect from the Cleveland Ironstone Formation (proximal location), Grey Shale Member (intermediate location), and Mulgrave Shale Member (distal location) (Figure 5.1). All the information about lithology, thicknesses of the individual units, and sample locations were recorded in these logs.

This part of the Cleveland Basin was specifically targeted because it is largely continuous, very well exposed in many locations, and allows direct correlation between different sedimentary units. Overall, all of the field work was carried out during six periods (May 2008, 4 days; June 2008, 2 days; August 2008, 1 day; February 2009, 4 days; July 2009, 3 days; November 2009, 2 days).

5.3. Sampling strategy

In order to investigate the small-scale (10^{-2} to 10^{-6} m) lithofacies variability in different parts of this succession, a total of 151 unweathered samples were collected from the three studied sections either from cliffs or from coastal wave-cut platforms. These mudstone samples were collected systematically either every 0.25 m or wheresoever there was an obvious change in lithofacies. Overall, sixty samples were collected from the Cleveland Ironstone Formation; fifty samples were collected from the Grey Shale Member; and finally forty one samples were collected from the Mulgrave Shale Member (Jet Rock).

All the collected 151 samples were sliced, slabbed, polished and large (40 × 60 mm) thin sections (20 to 25 µm thick) were prepared for petrographic investigations. The collected samples were prepared in this way in order to maximize their textural resolution (e.g. Macquaker, 1994a; Macquaker and Keller, 2005).

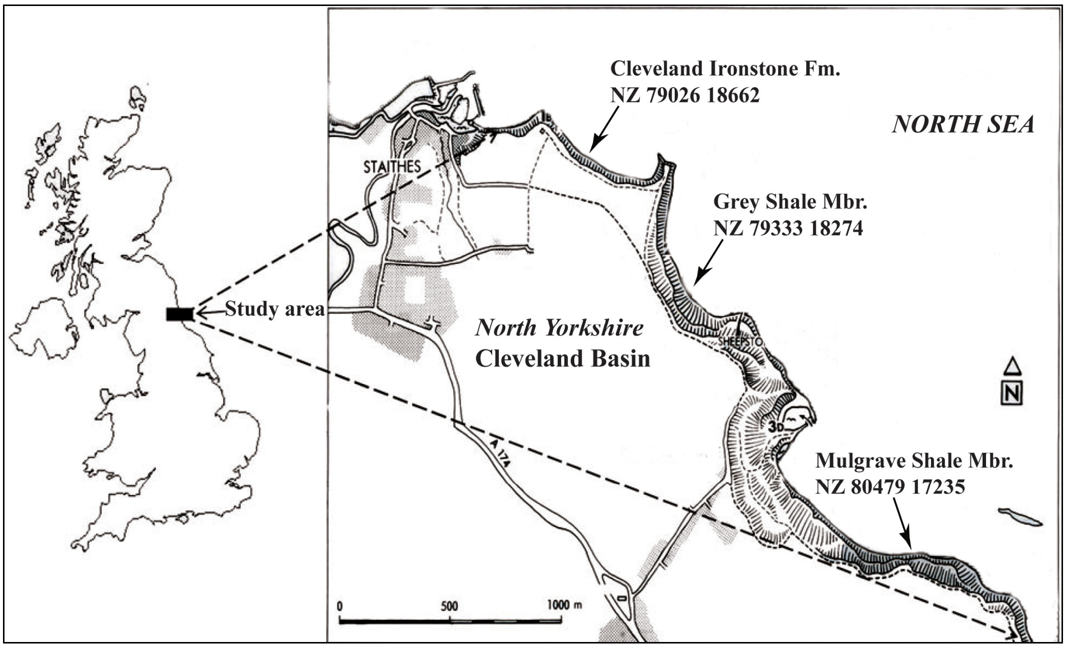

Figure 5.1. Map showing locations of the key exposures of the Cleveland Ironstone Formation, Grey Shale Member and Mulgrave Shale Member in the Cleveland Basin, UK. Modified after Rawson and Wright (1992).

5.4. Petrographic methods

All the petrographic analyses including thin-section preparations were performed at the Williamson Research Centre in the School of Earth, Atmospheric and Environmental Sciences, University of Manchester. Detailed information about thin section preparation and all petrographic analyses are presented below.

5.4.1. The preparation of thin sections

In order to identify processes responsible for the formation of individual beds, sediment dispersal and sediment disruption following deposition (bioturbation, and dewatering) unusually large normal to bedding polished thin sections were prepared utilizing standard procedures (e.g. Camuti and McGuire, 1999). In order to reduce sample damage in these soft, fine-grained, poorly cemented, clay-rich rocks, a non-aqueous coolant/lubricant medium (paraffin / kerosene) was utilized during the thin section preparation processes (e.g. Macquaker and Adams, 2003). In addition to the 151 samples that were prepared normal to bedding nine horizontal thin sections were also prepared parallel to bedding. Initially, each field sample was cut into a thin (1 to 2 mm thick) slab with dimensions (76 x 50 mm) using saws with continuous-rim diamond blades (8 cm in diameter). Where damage occurred during the slab manufacturing process, a cyano-acrylate adhesive was used to repair the sample. Once the integrity of the slab had been established, a selected face was then mechanically ground utilizing a full-faced rotating diamond grinding disc (100 µm particle-size silicon carbide abrasive powder). Finer grades of abrasive (60 µm to 12 µm) particle sized were then applied to the same surface. The ground slice surface was then attached to a pre-ground glass microscope slide with low-viscosity epoxy resins (epotek) that possess appropriate optical properties, and is described as "nil-bonding" – a property which allows the thickness of the resin between the glass and sample to be disregarded. Once a set of 12 samples had been mounted, the jig was then placed on a hot plate at 65°C in order to accelerate the resin curing time. After approximately 90 minutes the glass mounted samples were then ready to be machined. During this process the excess material from the glass thin section was cut off the slab using a Petro Thin (Buehler) sectioning system. After that, the thin section was carefully ground using the same machine close to its final thickness (20 to 25 µm). A fine polish was applied at this stage using a paper lap on a rotating plate loaded with diamond paste to remove any grinding damage and excess thickness. A highly polished surface can be produced utilising 1 µm polycrystalline diamond paste or solution.

During this operation, all grinding and polishing processes were carried out in oil in order to avoid hydration and sample disintegration (e.g. Macquaker and Taylor, 1996). All thin sections were prepared thinner than normal in order to maximize their textural resolution when analysed optically and electron-optically (e.g. Macquaker, 1994a; Macquaker and Keller, 2005).

5.4.2. Thin-section scan

To obtain details of 10^{-2} to 10^{-3} m-scale microtextures present all the thin sections were recorded by scanning the slides in a flat bed 35 mm slide scanner (Epson 1250) attached to a Dell microcomputer running Illustrator and Photoshop. Analyses at this scale is very important as it enables bed and laminae-geometries in these fine grained sediments to be imaged and it “fills the gap” between conventional handspecimen and thin section observations (e.g. DeKeyser, 1999).

5.4.3. Low-power optical microscopy

Following scanning, the fabrics present within individual beds and lamina-sets at 10^{-3} to 10^{-4} m-scales were determined utilizing transmitted optical microscopic methods (Nikon Labophot Pol), attached to a digital camera (Jenoptik Jena D-07739) to obtain details of the textural variability. The microscope was operated in both plane polarized and cross polarized light and approximately 20 photomicrographs were captured from each thin section at magnifications of × 2, × 4, × 10 and × 20.

5.4.4. Backscattered scanning electron microscopy

The mineralogy of the matrix fraction, textures and cement paragenesis were determined using higher resolution (10^{-4} to 10^{-5} m scale) JEOL 6400 scanning electron microscope (SEM) equipped with a backscattered electron detector (BSE), Link four-quadrant, and energy dispersive spectrometry (EDS). 140 uncovered and polished thin sections were firstly coated in carbon to prevent sample charging and achieve adequate conductivity. Then, each thin section was carried into a proper sample holder. In order to enhance image quality, small drops of silver dag were added to both ends of the holder to be sure that the conductivity throughout the surface of the sample is equal.

Approximately 15 BSE images from each thin section were captured at different scales (× 20, × 100, × 250, × 500, × 1000 and × 2500 magnifications) utilizing a Semafore digital framestore connected to the SEM. Where there was any doubt about mineral identification, a Link EDS detector attached to a Link EXL minicomputer was used. The SEM was operated at 20 kV and 2 nA, with working distance of 15 mm.

5.5. Whole rock Analytical Techniques

XRD analyses on all 151 samples were performed in the School of Earth, Atmospheric and Environmental Sciences, University of Manchester. TOC analyses on 151 samples were performed by the University of Newcastle (UK) and Manchester Metropolitan University (UK). Prior to these analyses, each sample was crushed utilizing a powered jaw-crusher and then ground using a vibro-mill in the Williamson Research Centre, University of Manchester.

5.5.1. XRD analyses

The whole rock mineralogy of each sample was determined using X-Ray diffractometry. The instrument used for this purpose was a Philips PW 1730 X-ray diffractometer. Before each analysis, a slurry mount of the sample was prepared from slurry of ca. 0.5 g of powdered sample with ca. 1 ml of amyl acetate and left to dry on a flat piece of glass, which then is inserted into diffractometer. The XRD was operated using Cu, K $\alpha 1$ radiation at 40 KV, 40 mA. The samples were scanned from 5-70° (2θ), with a step size of 0.02° (2θ) and a count time of 2 seconds per step.

5.5.2. Total Organic Carbon analyses

The total organic carbon contents (TOC) were determined from each sample. TOC analysis is important because these rocks are organic carbon rich and some units are potential source rocks (e.g. Tyson, 1995). These analyses were performed using powdered materials. Approximately 100 mg aliquots of the ground samples are weighed into LECO porous ceramic crucibles. After that, all the samples are decarbonated using 2-3ml aliquots of hot (~60C) 4M HCl, rinsed six times using three ml aliquots of deionized water, and then left in an oven at 60C° for at least 5 hours to dry. Using a LECO CS244 carbon analyzer, all the decarbonated and dried samples are then heated in a stream of oxygen, using an induction furnace, in order to oxidize the carbon and produce CO_2 which in turn is measured utilizing an infra-red detector. LECO analyser was calibrated using LECO standard carbon steel rings (1g, nominal carbon content 0.8%), and then the calibration was verified by analysis of a certified reference material (CRM).

5.6. Nomenclature used to describe Cleveland Basin sediments

Historically, most nomenclature schemes used to describe fine-grained sediments have been based upon their weathering characteristics rather than being based on detailed descriptions of their constituents. In order to generate comprehensive rock descriptions that include textural, mineralogical, grain size and grain components as well as to improve the opportunities to compare all fine-grained sediments with one and another, the predominantly siliciclastic fine-grained sediments of the Cleveland Ironstone Formation, Grey Shale Member and Mulgrave Shale Member (Jet Rock) were broadly described using the classification scheme outlined by Macquaker and Adams (2003).

The main aim of this scheme was to describe the variability within fine-grained sedimentary rocks directly based on any sedimentary structures present and the relative abundance of all constituents (allochthonous, autochthonous, and diagenetic) that form > 10% of the total volume. According to this nomenclature, mudstones are any sedimentary rocks that comprise more than 50% grains by mass that are less than 0.063 mm in size. Moreover, any mudstone containing more than 90% of a material is described as being 'dominated' by that constituent. In contrast where it contains between 50 and 90% of a material it is described as being 'rich' in that material, and where it contains between 10 and 50% it is said to be 'bearing' that constituent. These descriptions are then prefaced by terms that describe the main sedimentary fabrics present (e.g. "thin-bedded", "bioturbated", "laminated") to give a comprehensive name for a particular unit. Although this scheme is based on petrographic investigations, analytical (XRD) and geochemical (TOC) data as well as hand specimen scale attributes have also been included in the ultimate rock descriptions.

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Section 2:

Results

Chapter 6

Sediment transport processes in an ancient mud-dominated succession: a comparison of processes operating in marine offshore settings and anoxic basinal environments

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6.1. Abstract

Few studies describe and compare the transport mechanisms operating to disperse mud in different parts of basins. Instead, the physical processes operating to disperse mud in offshore environments, where storm and tidal processes are interpreted to dominate, are generally considered in isolation from those occurring in basinal settings where changes in bottom water anoxia and suspension settling from buoyant plumes are mostly interpreted to dominate. Using microtextural, mineralogical and geochemical data derived from the analyses of 151 thin-sections obtained from the Lower Jurassic mudstone-dominated succession exposed on the coast of northeast England, we investigate how varying sediment dispersal mechanisms, bioturbation and early diagenesis operated to produce the lithofacies variability observed. In particular we consider the processes of sediment delivery while bottom waters were interpreted to be euxinic.

Analyses of these samples reveal that the succession is highly variable at mm to cm scales. Six main lithofacies were observed: (1) sand- and clay-bearing, silt-rich mudstones; (2) silt-bearing, clay-rich mudstones; (3) clay-rich mudstones; (4) clay-, calcareous nannoplankton-, and organic carbon-bearing mudstones; (5) fine-grained muddy sandstones; and (6) cement-rich mudstones. These units are organised typically into stacked successions of sharp-based, normally-graded, thin (< 10 mm) beds. Individual beds exhibit a variety of sedimentary structures. Specifically tempestites, wave enhanced sediment gravity flows of fluid mud, ripples and gutter casts are common in the coarser-grained mudstone facies. In contrast, thin siltstone lags, compacted ripples and organo-minerallic aggregates are common in the finer grained mudstone facies and those with significant primary production-derived components. Bioturbation is common throughout.

These data indicate that sediment was transported by density flows and traction currents operating at the sediment-water interface in all parts of the studied succession. Bioturbation has overprinted depositional fabrics in the majority of samples. The extent to which persistent bottom water anoxia and low energy suspension settling influenced lithofacies variability in the basinal parts of the succession has been overstated; these environments were more dynamic than most researchers have previously concluded.

6.2. Introduction and aims

Fine-grained sedimentary rocks, with an average grain size <62.5 µm (e.g. "shales"), are the most common (>60%) sedimentary rock types at the Earth's surface (e.g. Aplin and Macquaker, 2010). These rocks typically preserve the most complete stratigraphic record in sedimentary basins, are important economically in conventional hydrocarbon plays as sources and seals (e.g. Tissot and Welte, 1989; Schieber, 1999; Bohacs et al., 2005) and act as reservoirs in unconventional "shale gas" plays (e.g. Aplin and Macquaker, 2010). Detailed analyses of these sediments, particularly using data derived from geochemical proxies, have provided the geological community with a better understanding of the conditions under which they were deposited (e.g. Raiswell, 1988; Raiswell et al., 1988; Canfield, 1989; Bohacs et al., 2005; Wignall et al., 2005; Algeo and Lyons, 2006). Data derived from proxy techniques however, provide little direct insight into the mechanisms of sediment dispersal because textural information is typically not collected during these studies and these rocks typically exhibit little obvious variability, beyond exhibiting lamination, in hand specimen.

Thin sections prepared from these materials enable a great deal of microtextural variability to be observed (e.g. Schieber, 1990; Macquaker and Gawthorpe, 1993; O'Brien, 1996; Macquaker and Keller, 2005; Macquaker et al., 2007) and demonstrates that they are much more heterogeneous than most researchers have previously determined on the basis of handspecimen-scale observations. These textural data provide insights into the physical processes responsible for mud dispersal prior to deposition and the effects of bioturbation after the sediment has been deposited (e.g. O'Brien, 1990; Macquaker et al., 1998; Schieber, 2003; Macquaker and Bohacs, 2007; Schieber et al., 2007; Schieber and Southard, 2009). In many instances, they demonstrate that (1) mudstones described as laminated on the basis of field description are actually thin-bedded and the products of individual depositional events separated by breaks in sediment accumulation (e.g. Campbell, 1967; Macquaker and Taylor, 1996), (2) the sediment commonly contains evidence of deposition from traction and density currents rather than being deposited from suspension settling (e.g. Wignall et al., 2005; Macquaker and Bohacs, 2007; Macquaker et al., 2010a), and (3) a diminutive infauna appears to have disrupted the original sediment fabrics (e.g. Macquaker and Taylor, 1996). In addition, recent physical modelling studies (e.g. Lamb and Parsons, 2005; Schieber et al., 2007; Schieber and Southard, 2009) provide significant new insights into the hydrodynamic behaviour of mud-sized material in subaqueous environments and the products of many of these experiments are similar to the microtextures observed in thin-section.

Clastic lithofacies distributions on continental shelves are controlled by a complex interplay between the effects of waves, currents, gravity and biological reworking (e.g. Aigner and Reineck, 1982; Swift et al., 1986; Duke et al., 1991; Cheel and Leckie, 1993). In coarse clastic successions the products of these processes are well known and how these processes interact in different areas of the shelf are well understood. The study of facies distributions in the fine-grained portions of these successions has mostly been less exhaustive. Over the last few decades researchers have begun to demonstrate that lithofacies belts can also be recognised in muddy depositional settings on shelves and that the interplay of similarly complex suite of processes, including suspension settling (e.g. DeMaster et al., 1986; Nittrouer et al., 1986; Alldredge and Gotschalk, 1990), bottom water anoxia (e.g. Wignall and Hallam, 1991; Wignall et al., 2005), wave-enhanced gravity flows of fluid mud (e.g. Wright et al., 2001; Friedrichs and Wright, 2004; Traykovski et al., 2007), storms and tides (e.g. Swift, 1985; Swift et al., 1986), likely control facies distributions in these settings too.

To complicate matters further, mudstone-dominated successions are typically interpreted in very different ways depending upon their field appearance, grain size, total organic carbon contents and degree of fissility. For instance, it is commonly argued that fine-grained, fissile organic-carbon-rich mudstones with small pyrite framboids (e.g. "black shales") were deposited in distal, "basinal settings" where sediment was delivered by suspension settling from buoyant plumes, with variations in bottom water oxygen concentrations and primary organic carbon production operating to control lithofacies variability (e.g. Didyk et al., 1978; Tourtelot, 1979; Van Buchem and McCave, 1989; Stow et al., 2001; Wignall et al., 2005). In contrast, less fissile, coarser mudstones are typically interpreted, in a similar manner to sandstones deposited further updip, with storms, tidal activity and burrowing being the main dispersal and fabric modifying processes (e.g. Hourbolt, 1968; McCave, 1971; Fursich and Oschmann, 1986; Macquaker et al., 2007; Lamb et al., 2008).

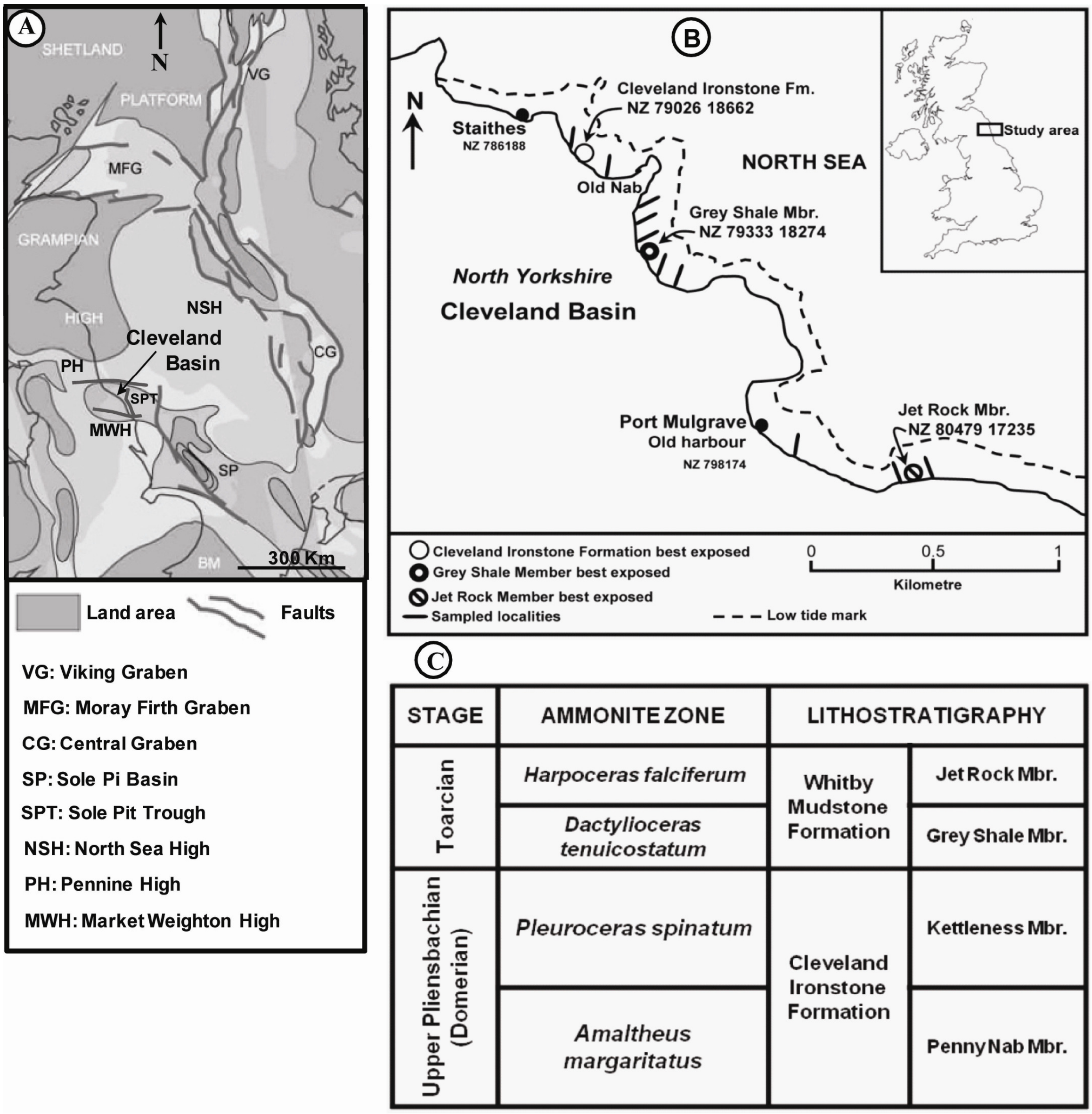
Few studies, however, document the systematic textural variability in mudstones deposited in different parts of the same basin, particularly where the bottom waters are prone to becoming persistently anoxic. This study aims to investigate (using combined petrographic and geochemical techniques), and compare the sedimentological processes responsible for fine-grained sediment production and dispersal in such a basin. The natural laboratory chosen for this research includes Lower Jurassic aged strata preserved in the Cleveland Basin in Northeast England.

The study analyses material collected from the Lower Jurassic succession that includes the Cleveland Ironstone Formation, the Grey Shale and Mulgrave Shale (formerly Jet Rock) Members of the Whitby Mudstone Formation exposed on the North Yorkshire Coast, England (Figure 6.1). This succession was specifically chosen because it is well-exposed, lacks major unconformities and has been extensively studied by others investigating the origins of the Toarcian Anoxic Event, extinction episodes associated with this event, and the role of micro-organisms in early diagenesis (e.g. Howarth, 1955, 1962, 1973; Greensmith et al., 1980; Rawson et al., 1983; Rawson and Wright, 1992; Hesselbo and Jenkyns, 1995; Macquaker and Taylor, 1996; Rawson and Wright, 1996; Sælen et al., 1996; Rawson and Wright, 2000; Kemp et al., 2005; Wignall et al., 2005; McArthur et al., 2008; Caswell et al., 2009).

6.3. Geological background

Located on the western margin of the extensional North Sea Basin system, marine deposition in the Cleveland Basin (Figure 6.1A) was initiated during the late Triassic (Rawson and Wright, 1996). Regional extension, associated with the earliest opening of the North Atlantic, led to the development of a basin over North Yorkshire that was connected to the Sole Pit Trough in the East. The basin is defined by the North Sea High to the northeast, the Pennines in the west and by the Market Weighton High to the south (Rawson and Wright, 1996; Powell, 2010). During the early Jurassic, a thick succession of marine sediment, dominated by siliciclastic mudstones began to accumulate.

The Cleveland Ironstone Formation (25 m thick) is dominated by coarse-grained siliciclastic mudstones, with some calcareous concretionary units, very fine-grained muddy sandstones and sideritic and chamositic, shelly ironstones that cap overall upward-coarsening successions (e.g. Rawson et al., 1983; Rawson and Wright, 1992; Macquaker and Taylor, 1996). The presence of gutter casts, wave ripple laminae, distal tempestites and interbedded units composed variously of mudstones and sandstones has led researchers to conclude that these units were likely deposited on a storm dominated marine shelf. The obvious cyclicity in this part of the succession was likely formed in response to relative changes in sea-level (e.g. Rawson et al., 1983; Macquaker and Taylor, 1996).



STAGE	AMMONITE ZONE	LITHOSTRATIGRAPHY	
Toarcian	*Harpoceras falciferum*	Whitby Mudstone Formation	Jet Rock Mbr.
	Dactylioceras tenuicostatum		Grey Shale Mbr.
Upper Pliensbachian (Domerian)	*Pleuroceras spinatum*	Cleveland Ironstone Formation	Kettleness Mbr.
	Amaltheus margaritatus		Penny Nab Mbr.

Figure 6.1. A) Palaeogeographic map of the Cleveland Basin and coastline of NE England (modified from Ziegler, 1990). B) Map showing locations of key exposures of the Cleveland Ironstone Formation, Grey Shale Member and Jet Rock of the Mulgrave Shale Member. C) Stratigraphy of the studied interval (Rawson and Wright, 1992).

The Whitby Mudstone Formation (c. 22 m thick) overlies the Cleveland Ironstone Formation. The Grey Shale Member forms the basal c.13 m of the Whitby Mudstone Formation. The majority of the Grey Shale Member comprises bioturbated mudstones that contain thin sharp-based beds and locally, wave ripple and starved ripple laminae (Wignall et al., 2005). Locally, at Kettleness (approximately 5 km to the north east of the study area), hummocky cross stratification has been identified in a silt-rich unit towards the top of this interval (Wignall et al., 2005). Prominent bands of calcareous and sideritic nodules are also present in this unit (Howarth, 1973; Rawson and Wright, 1996). At the top of this unit, bioturbation intensity and grain size both decrease, laminae are better preserved and populations of very small pyrite framboids are present in the sediment (Wignall et al., 2005). The extensive bioturbation and presence of hummocky cross stratification in the majority of this unit indicates that it was likely deposited on the distal portions of a mud-dominated marine shelf where storm waves at least occasionally reworked the sediment and the bottom waters were predominantly either oxic or dysoxic (Wignall et al., 2005), with deposition in the top part of the unit occurring under conditions of bottom-water anoxia.

The top part of the Grey Shale Member and the overlying c. 8 m thick Mulgrave Shale Member are dominated by very fine-grained, laminated, organic-carbon-rich mudstones with thin bands of calcareous nodules (e.g. Pye and Krinsley, 1986; Rawson and Wright, 1996; Kemp et al., 2005; Wignall et al., 2005). These units exhibit well preserved lamination (see Myers and Wignall, 1987) and contain significant amounts of pyrite, much of which is organised into diminutive framboids (Raiswell and Berner, 1985; Wignall and Newton, 1998). The transition from the Grey Shales to the overlying Mulgrave Shale Formation is interpreted to coincide with an increase of water depth in the basin with background sedimentation occurring likely via suspension settling in low-energy conditions where bottom-water anoxia existed (e.g. Pye and Krinsley, 1986; Wignall, 1991; Sælen et al., 1996; Hallam and Wignall, 1997; Sælen et al., 2000; Wignall et al., 2005). The boundary between the Grey Shale and Mulgrave Shale members broadly coincides with one of the most severe mass extinction anoxic events in the Mesozoic Era (e.g. Wignall, 1991; Wignall et al., 2005; McArthur et al., 2008; Wignall and Bond, 2008; Caswell et al., 2009).

6.4. Methods and terminology

In order to determine the lithofacies variability present in this mudstone-dominated succession, the coastal exposure between Staithes and Port Mulgrave (Figure 6.1B) was logged and sampled (Figure 6.2). Fresh samples were collected either from the wave cut platform or from shallow pits excavated in the local sea cliffs. In total, 151 samples were collected at vertical intervals of approximately 0.3 m (Figure 6.2). To acquire microtextural data, unusually thin (20 to 25 μm) polished sections were prepared from each sample.

Details of 10^{-2} to 10^{-3} m-scale textures present in each thin section were obtained by scanning the thin sections in a flat bed 35 mm film scanner (Epson 1250). Their textural attributes were then analysed using a conventional optical microscope (Nikon Labophot Pol) to obtain details of the 10^{-3} to 10^{-4} m-scale textures, coated in carbon and then analysed again using a JEOL 6400 scanning electron microscope (SEM) equipped with backscattered electron (BSE) detector and fully quantitative Link eXL energy dispersive (ED) analytical system to obtain details of 10^{-4} to 10^{-5} m-scale textures. To confirm the mineralogy, all the samples were disaggregated, sedimented on slides, and analysed using X-Ray diffraction techniques (XRD). X-ray diffraction analyses were performed on a Bruker D8 Advance diffractometer. The total organic carbon (TOC) content of each sample was determined using a Leco C/S carbon/sulphur analyzer after removal of any mineralized carbon by acidification. The field, petrographic and geochemical data were combined to produce composite lithofacies descriptions.

The lithofacies present are described using the nomenclature scheme of Macquaker & Adams (2003). Individual beds are described on the basis of grain size, grain origin (allochthonous, autochthonous and diagenetic) in addition to their constituent laminae and bedding geometries (after Campbell, 1967). In this nomenclature a mudstone that is composed of >90% of a particular component is described as being “dominated” by that constituent, a rock that contains 50-90% of a particularly component is described as being “rich” in that constituent, and one that contains 10-50% is described as “bearing” that constituent. This nomenclature scheme allows the subtleties of different mudstone types to be described enabling some of the processes responsible for sediment deposition and subsequent disruption to be recognised.

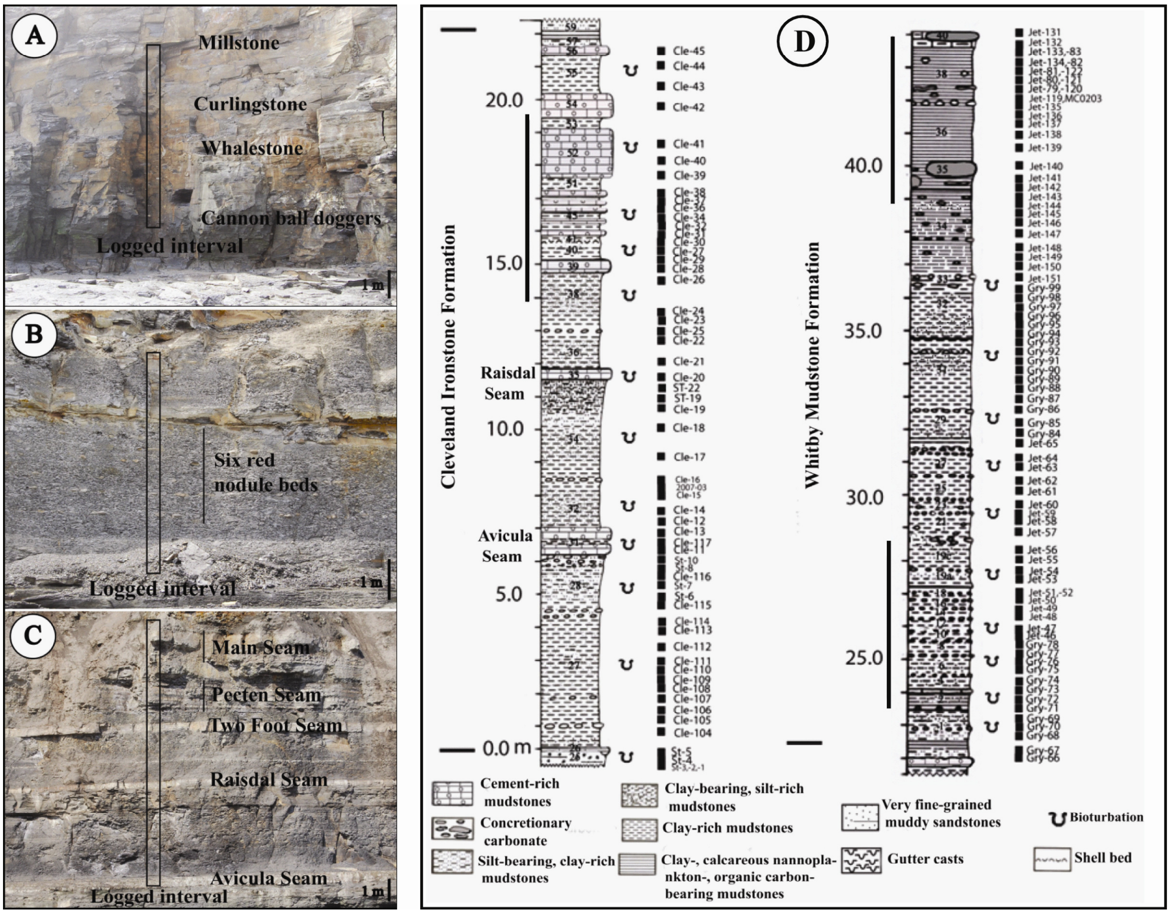


Figure 6.2. Field photographs and logged intervals showing outcrop expression of the studied succession: A) Jet Rock of the Mulgrave Shale Member; B) Grey Shale Member; C) Cleveland Ironstone Formation; D) Details of two logged and sampled successions through the Cleveland Ironstone Formation and Whitby Mudstone Formation, showing bed numbers (within log from Howarth, 1955), sample numbers (to right of log) and mudstone lithofacies. Logs modified after Howarth (1992), Rawson & Wright (1996).

6.5. Mudstone lithofacies

Six main mudstone lithofacies types are identified. Their broad stratigraphic distributions (Figure 6.2) are described herein: (1) sand- and clay-bearing, silt-rich mudstones are rare, and only described from strata immediately below some of the cement-rich mudstones in the Cleveland Ironstone Formation; (2) silt-bearing, clay-rich mudstones are common in our samples from the Cleveland Ironstone Formation and form a subordinate component of the Grey Shales Member; (3) clay-rich mudstones are common in the Grey Shales Member and the lower part of the Mulgrave Shale Member and only rare encountered in the Cleveland Ironstone Formation; (4) clay-, calcareous nannoplankton-, organic-carbon-bearing mudstones are common in the Mulgrave Shale Member and rare in the upper Grey

Shales Member; (5) fine-grained muddy sandstones are sparse in the studied succession and only described from the base of the Cleveland Ironstone Formation; and (6) cement-rich mudstones are widely encountered and are present as relatively thin (up to 0.5 m thick) units throughout the succession.

In addition to exhibiting grain size variability, these mudstones also contain a variety of microtextures including: parallel lamination, wave- and current-ripple beds, gutter casts, and intraformational conglomerates. In much of the succession, however, the majority of the primary fabrics have been either completely or partially overprinted by the burrowing activities of an infaunal community. Detailed descriptions of each lithofacies are presented below.

6.5.1. Sand- and clay-bearing, silt-rich mudstones

These mudstones are organised into sharp-based, normally-graded thin beds (5-40 mm) (Figure 6.3). Some units contain gutter casts (Figure 6.3A) (Greensmith et al., 1980; Rawson and Wright, 1992). Where preserved, laminae exhibit both discontinuous wavy geometries and curved non-parallel, concave-up geometries and typically lap down onto underlying bedding planes (Figure 6.3B). Bioturbation has disrupted much of the primary fabrics, particularly towards the tops of the individual beds (Figure 6.3C). Bioturbation here is attributed to *Chondrites isp*., *Phycosiphon isp*. and *Planolites isp*.

The detrital sand and silt-sized components of these beds are mainly composed of quartz, minor feldspar and muscovite (Figure 6.3D). In addition, these units also contain reworked and comminuted fossil debris derived from echinoderm, foraminifer and bivalve tests (Figure 6.3B). These coarse-grained components are preserved in a matrix of clay minerals including kaolinite and illite, chamosite, fine-grained apatite, siderite, pyrite and amorphous organic matter (TOC average 1.0%, range 0.5-1.8%).

Figure 6.3. (see next page) Sand- and clay-bearing silt-rich mudstone. A) Field photograph of unit below Raisdale Seam (see Figure 6.2) illustrating normally graded thin beds and gutter casts (arrow). B) Thin-section scan of St-19. This sample contains normally graded thin beds with silt-rich bases and clay-rich tops, fragmentary shell debris (arrow). C) Thin-section scan of homogenised unit (St-22). Note the presence of a basal erosional surface, and bioturbation. D) BSE image of Cle-19 illustrating fine sand and silt grains (composed

mainly of detrital grains of quartz, feldspar and muscovite) preserved in a matrix of clay minerals, minor pyrite and amorphous organic matter.

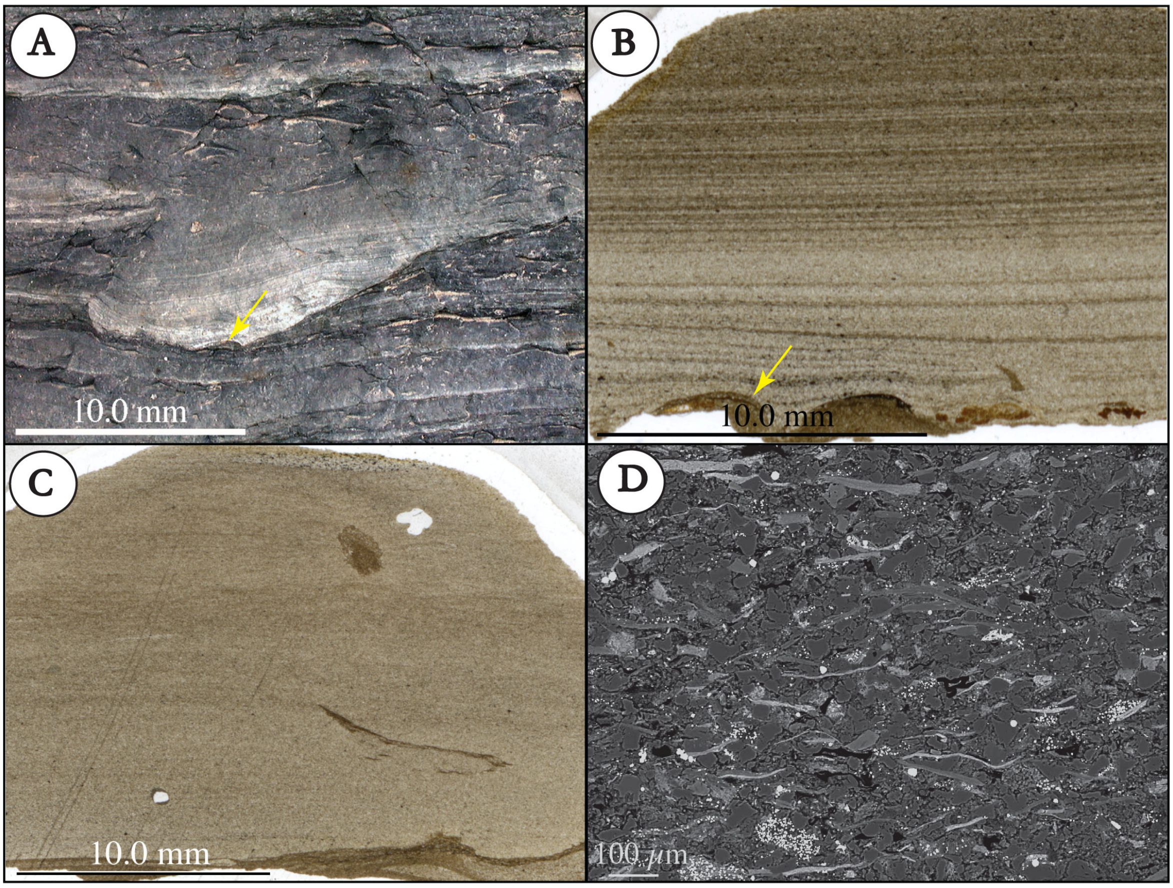


Figure 6.3. (see caption in previous page)

6.5.2. Silt-bearing, clay-rich mudstones

They are typically organised into stacked successions of thin (5-20 mm), normally graded sharp-based beds (Figure 6.4A). Individual beds either exhibit lamination, are partially burrowed (attributed to a combination of *Phycosiphon isp*, *Planolites isp.* and *Chondrites isp.*) or completely homogenised. Where preserved, lamina geometries vary from being continuous parallel and wavy, to non-parallel and curved (Figure 6.4B, C). Internally the beds commonly exhibit a triplet motif of an homogenous basal laminaset (with rare concave-up curved lamina), abruptly overlain by a laminaset of intercalated wavy and parallel laminae composed of layers of silt and clay, overlain by a normally graded clay laminaset (Figure 6.4B, C).

The silt-grade fraction in these mudstones is composed of quartz, some K-feldspar and muscovite. These framework materials are preserved in a matrix of clay-sized materials that include a mixed mineral assemblage of kaolinite and illite-smectite, small regions of carbonate cement (some calcite, minor siderite) in addition to minor amorphous organic matter (TOC average 1.2%, range 0.5 to 3.6%). Both framboidal and euhedral pyrite is visible (Figure 6.4D). Reworked and disarticulated shell debris is also present as discontinuous lags at bed bases and dispersed as individual tests throughout the beds.

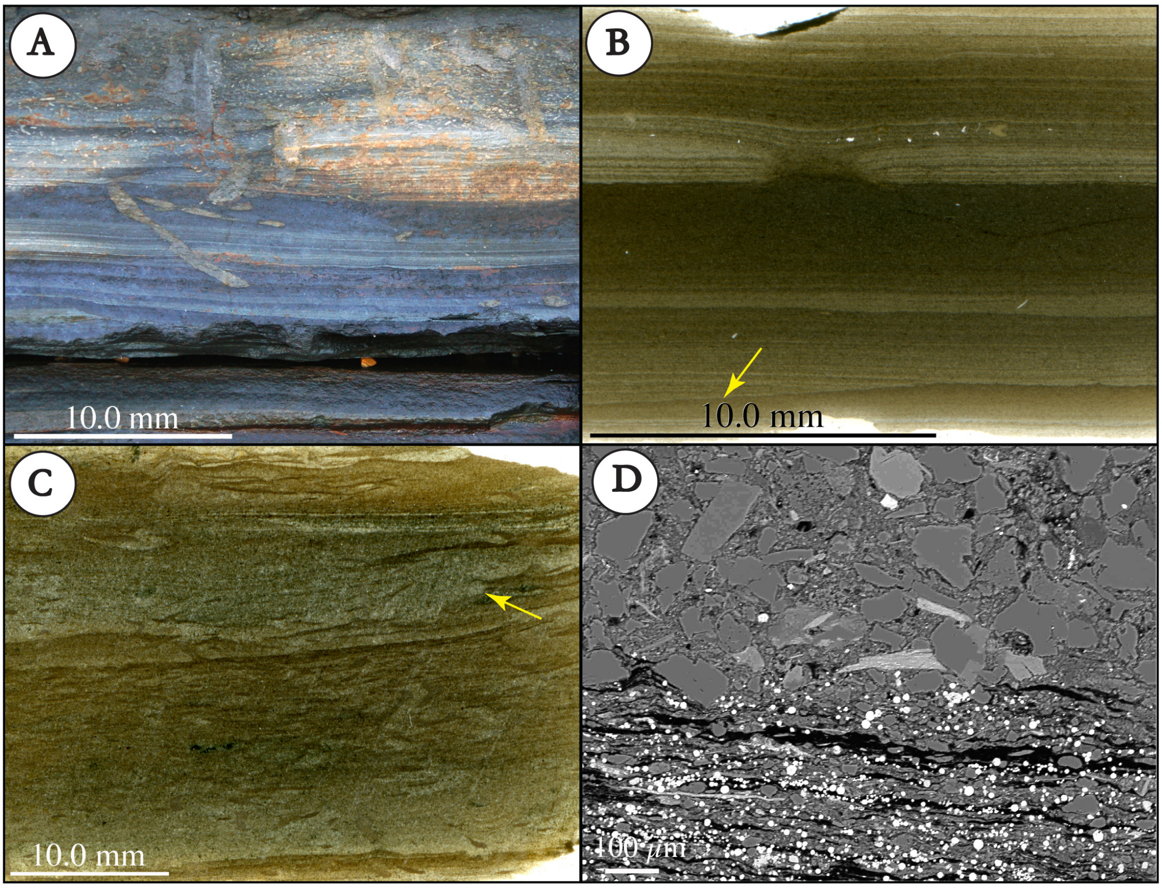


Figure 6.4. Silt-bearing, clay-rich mudstones. A) Field photograph of the base of the Grey Shale Member illustrating a stacked succession of normally graded thin beds with erosional bases and bioturbated tops. B) Thin-section scan of Gry-84. This sample contains thin (<10 mm) beds with erosional bases (arrow). Individual beds are normally graded and exhibit basal silt-rich laminae, that are initially overlain by continuous intercalated silt and clay-rich laminae and ultimately draped by bioturbated, clay-rich laminae. C) Thin-section scan of Cle-18. This sample contains normally graded thin beds bounded by erosional surfaces (arrow). Some wavy and continuous laminae are preserved; elsewhere the laminae are disrupted by *Phycosiphon isp*. and *Chondrites isp*. D) BSE micrographs of sample Gry-84. This sample illustrates silt sized quartz grains in a matrix of clay, amorphous organic matter and pyrite.

6.5.3. Clay-rich mudstones

Clay-rich mudstones are organised into stacked successions of thin (2-20 mm) beds that are bounded by a range of even, parallel, wavy, and discontinuous bedding planes (Figure 6.5A, B). Some of these units contain dispersed reworked fragmentary shell debris (Figure 6.5C). Internally, most beds have been homogenised by organisms colonizing the sediment (e.g. *Phycosiphon isp*, *Planolites isp.* and *Chondrites isp.*) (Figure 6.5B). Where laminae are visible, however, they exhibit continuous parallel, wavy, to non-parallel and curved geometries that, in spite of being compacted, lap down onto underlying bedding planes.

The clay-rich mudstones comprise minor silt-sized material and fragmentary shell debris preserved in a matrix of clay minerals that mainly comprise kaolinite, muscovite, illite, some calcite and siderite cements, and minor clinochlore (Figure 6.5D). Pyrite is present as dispersed framboids and euhedral forms associated with amorphous organic matter (TOC average 2.7%, range 0.6 to 8.6%).

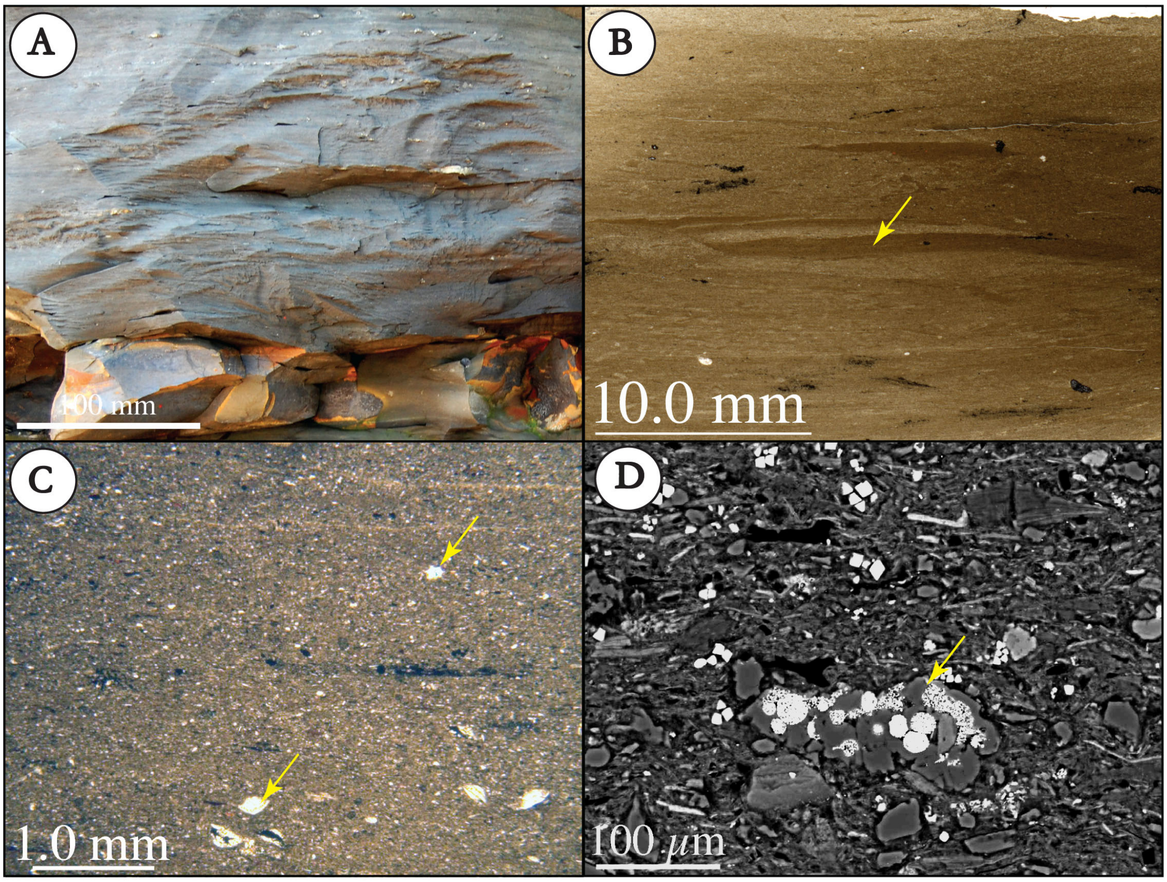


Figure 6.5. Clay-rich mudstones A) Field photograph of units between Avicula and Raisdale seams (Figure 6.2). Note the presence of stacked thin (2-20 mm) beds bounded

by even, parallel, wavy and discontinuous bedding planes. B) Thin-section scan of 2007-03. This sample is homogenised by bioturbation attributed to *Phycosiphon isp*. (arrow). C) Optical micrograph of sample Gry-88 illustrating silt material preserved in a matrix predominantly composed of clay, pyrite, organic matter, and some fragmentary shell debris (echinoderm tests, arrowed). D) BSE micrograph of Gry-88 illustrating silt sized quartz in a matrix of clay, pyrite and amorphous organic matter. Note the presence of agglutinated benthic foraminifer with framboidal pyrite infilling shelter porosity (arrow).

6.5.4. Clay-, calcareous nannoplankton-, organic carbon-bearing mudstones

These mudstones are typically organised into thin (3-10 mm) sharp-based beds (Figure 6.6A), many of which contain thin silt lags at their bases. Lamination is commonly preserved at the bases of these beds (Figure 6.6B) in contrast to their tops which are commonly homogenised. Lamina geometries vary from continuous-planar parallel to discontinuous wavy non-parallel. In the laminated portions of the beds, flattened organo-minerallic aggregates composed of organic carbon, clay minerals, and coccolith-rich faecal pellets are common (Figure 6.6C).

The matrix component of these units comprises silt-sized grains of quartz, minor K-feldspar and detrital muscovite (Figure 6.6D). These components are preserved in a fine-grained matrix of clay minerals with some calcite, dolomite, minor siderite, pyrite and amorphous organic matter (TOC average 6.2%, range 3.2 to 14.2%). In these units, burrowing is attributed to a combination of *Planolites isp*. and *Phycosiphon isp*. Calcareous macrofossil debris (mainly bivalves) is composed of disarticulated tests.

6.5.5. Fine-grained muddy sandstone

This lithofacies forms units up to 0.2 m thick that exhibit symmetrical ripple laminae, wavy laminae and gutter casts. Internally, individual units are either (1) homogenous and burrowed or (2) organised into sharp-based thin beds that contain preserved lamination at their bases and exhibit bioturbated tops. Individual laminae that are curved and non-parallel typically lap down onto underlying bedding planes as ripple foresets. Bioturbation is attributed to a combination of *Chondrites isp., Phycosiphon isp.* and the burrows of an unidentified community of infaunal organisms.

The fine-grained sand and silt framework components are mainly composed of quartz, with some K-feldspar, detrital muscovite and crushed bivalve shell debris. These components are preserved within a matrix predominantly composed of clay minerals, as well as calcite and some pyrite cements. Minor amorphous organic matter is present in the matrix (TOC average 0.2%, range from 0 to 0.4%).

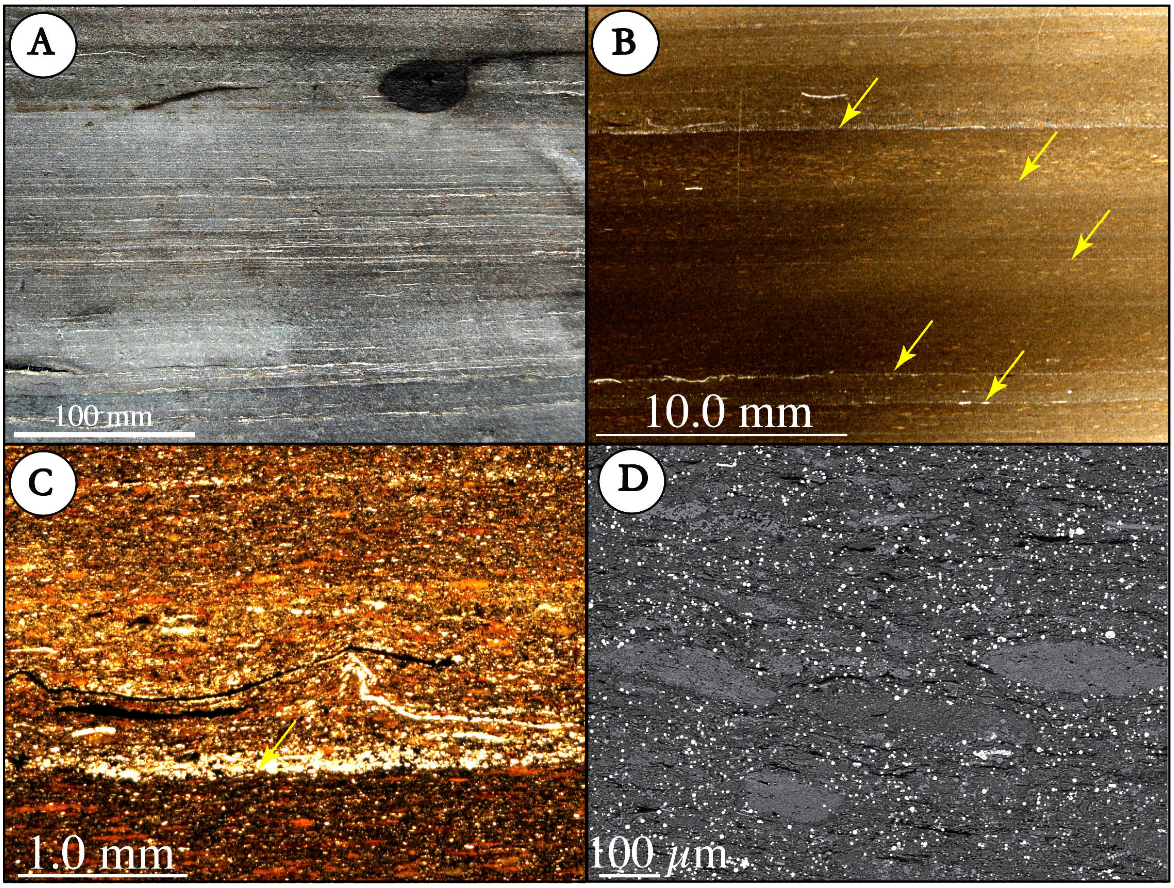


Figure 6.6. Clay-, calcareous nannoplankton-, organic carbon-bearing mudstones A) Field photograph (NZ 80479 17235) illustrates thin continuous beds with parting spacing less than 3 mm. B) Thin-section scan of MCO2O3, illustrating flattened organo-minerallic aggregates composed of organic carbon and coccolith-rich faecal pellets. Also note the presence of basal microscours (arrows). C) Optical micrograph of MCO2O3. Note that the individual laminae are composed of thin silt-rich partings (arrow) intercalated with clay and organic carbon-rich partings. D) BSE image of MCO2O3. The sample comprises silt-sized framework grains and a matrix predominantly composed of clay minerals (mainly kaolinite and illite), calcite as coccoliths, dolomite, minor siderite and pyrite cements.

6.5.6. Cement-rich mudstone

The concretionary carbonate horizons are distinctive in the field as they are more resistant to weathering than other lithofacies types. Some contain large (up to 0.2 m) grain and matrix supported intraclasts enclosed by chamosite ooids and very fine-grained silt-bearing sandstones and sand-bearing silt-rich mudstones. Four different sub-facies of cement-rich mudstones are present, each described below.

(1) Silt-bearing, siderite and ferroan calcite cement-rich mudstones form units <0.4 m thick. These units are organised into either normally-graded thin (<10 mm) beds or are homogenised. Burrowing is attributed to a combination of *Phycosiphon isp.* and *Chondrites isp*. The early siderite in these strata is typically enclosed by later non-ferroan calcite and minor pyrite cements. In addition, these units also contain a silt–sized fraction that is mainly composed of quartz and feldspar, with minor authigenic kaolinite infilling grain dissolution porosity (after feldspar).

(2) Silt-bearing siderite/chamosite ooidal and calcite cement bearing ironstones occur in weathering resistant units up to 1.0 m thick. These “ironstones” are typically pervasively bioturbated (*Rhizocorallium isp*., *Chondrites isp*., *Planolites isp.*). Locally, they contain abundant fragmentary shell debris composed of foraminifer, bivalve (oyster and clam) and echinoderm tests. Siderite occurs both as large areas of pore-filling cement that enclose chamosite ooids, and as small, zoned rhombohedra within the chamosite matrix. Zoned, non-ferroan calcite and pyrite cements are also present. These may either enclose or be enclosed by siderite. The detrital matrix in these units comprises silt-sized material, mainly composed of quartz, feldspar, muscovite with rare kaolinite infilling grain dissolution porosity, and amorphous organic matter (TOC average 2.9%, range 0.5 to 6.9%).

(3) Highly bioturbated silt-, hydroxyapatite- and siderite-cement bearing mudstones form units up to 0.15 m thick. These units are predominantly composed of detrital silt in addition to siderite and microcrystalline hydroxyfluorapatite cements. In addition, some quantities of chamosite are present. Hydroxyapatite cement encloses the chamosite grains. The silt fraction here is mainly composed of quartz and detrital mica, minor clay-sized material mainly composed of kaolinite, broken shell fragments, and trace amounts of pyrite.

(4) Bioturbated siderite cement-rich and calcite cement-rich mudstones with only minor silt and clay-sized components form discontinuous concretionary units located mainly within the clay-rich mudstone parts of the succession. They are predominantly composed

of coalesced siderite rhombohedra or microcrystalline calcite and pyrite cement masses. These cements precipitated in an uncompacted clay mineral matrix mainly composed of illite smectite, kaolinite, broken shell fragments and trace amounts of organic matter. Much of the silt component in these units is incorporated into the tests of agglutinated foraminifera and composed of quartz.

6.6. Interpretation and discussion

6.6.1. Fine-grained sediment production, delivery and accumulation

In this succession, most of the siliciclastic clay, silt and sand-sized components are likely derived from detrital inputs to the basin. These materials were most probably formed in palaeo-soil profiles that existed in the surrounding drainage catchments (e.g. Chamley, 1989), prior to being eroded and then delivered to the basin by rivers. A smaller proportion of the sediment overall, although a significant fraction of some of the mudstone units rich in clay-sized material in the Mulgrave Shale Member, comprises biogenic components. These include comminuted calcareous skeletal materials derived from bivalves, ammonoids, echinoderms, coccoliths, calcispheres, and foraminifera, in addition to organic carbon (e.g. Sælen et al., 1996; Sælen et al., 2000; Wignall et al., 2005; Kemp et al., 2006). The systematic temporal differences in grain size and composition identified here and by others (Macquaker and Taylor, 1996; Wignall et al., 2005), suggest that the balance of primary biogenic production relative to dilution and length of the sediment transport path varied during deposition of this succession. Specifically, it is likely that the coarser intervals towards the base (i.e. the fine-grained muddy sandstones**,** sand- and clay-bearing, silt-rich mudstones, and silt-bearing, clay-rich mudstones in the Cleveland Ironstone Formation and coarser intervals of the Grey Shales Member; e.g. Figures 6.3, 6.4) were deposited in more proximal settings, where primary production components were diluted by detrital clastic inputs (up to 3.6% organic matter, average 1.3%). In contrast, those units towards the top of the succession, where the lithofacies contain greater proportions of detrital clay and production-derived materials (i.e. clay-rich mudstones and clay-, calcareous nannoplankton-, organic carbon-bearing mudstones in the Mulgrave Shale Member; e.g. Figures 6.5, 6.6), were likely deposited in settings where clastic dilution of the production-derived components was less pronounced (up to 14.2% organic matter, average 5.0%).

The preserved microtextural information in these mudstones provides significant insights into sediment delivery mechanisms and the process that subsequently disrupted the sediment after deposition. The majority of mudstones sampled here are organised into units of thin (<10 mm), erosionally based beds that are normally graded. Many of these beds contain ripples, starved ripples or parallel lamination. On continental shelves, in the absence of any significant slopes, the processes responsible for these textures are likely to have been episodic, waning storm-induced combined flows (e.g. Kuehl et al., 1990; Nittrouer and Wright, 1994; Martin et al., 2008; Plint et al., 2009). There are a number of different microfabric styles present within these mudstones. For example, in coarser mudstones preserved towards the base of the succession, lamination is poorly developed and normal grading with homogenized tops is the dominant bed motif (Figure 6.3). These simple graded beds were likely deposited from episodic, waning currents that were initially erosional and had a small advective, traction-transport component, with deposition occurring from a turbulent flow as ambient energies waned. These units are interpreted to be analogous to the distal "tempestite deposits" recognised by many workers in offshore mudstone successions (e.g. Aigner and Reineck, 1982; Fursich and Oschmann, 1986; Swift et al., 1986; Dumas et al., 2005). Following deposition of these beds there was commonly sufficient time for the tops of these units to be colonized, prior to emplacement of the next event. Event deposition, followed by colonization produces the "lam-scram" fabrics of Goldring et al. (1991) (Figure 6.4). Very similar, albeit thinner, units have also been identified in the finer grained mudstones preserved towards the top of the succession. Here too, the mudstones are commonly organised into thin, normally-graded beds with sharp, scoured bases overlain by silt-rich laminae grading upwards into more clay-rich, pelleted laminae and with homogenised bed tops (Figure 6.6). The presence of these fabrics suggests that the sediment in the more distal parts of the succession was delivered by episodic waning flow events at the sediment-water interface. Additionally, as some of these units contain starved, low-angle ripple lamination, it is likely that even here, sediment-transport processes had an advective, traction-transport component (e.g. Schieber, 1990, 1998, 1999). These structures suggest that the fine-grained "basinal" mudstones that make up the Mulgrave Shale Member were not simply deposited from buoyant plumes by quiet-water suspension settling and certainly not always in low-energy settings. Wignall et al. (2005) documented a similar fabric (their Figure 4), however, they interpreted this fabric to be a product of compaction of a laminated silt-rich unit within a succession dominated by clay that was deposited by "background sedimentation" rather than as the product of a waning traction-flow deposit. While we agree that compaction has had a major effect on these sediments, the presence of laminae that lap down on to the underlying bedding plane, finely interbedded coarser and finer laminae that closely resemble fabrics produced in flume experiments and observed in other organic carbon-rich mudstones (Schieber et al., 2007; Macquaker and Bohacs, 2007), and the overall upward-fining motif indicate that these are better interpreted as ripples rather than as a partially laminated fabric that was a product of "background sedimentation" modified by compaction.

Although the overall normally graded "tempestite" motif is common throughout the studied interval, two distinctive fabrics are present that suggest that the processes responsible for traction flow transport varied at least spatially within the basin. In the coarser muddy sandstones and clay- and sand-bearing, silt-rich mudstones (e.g. Figure 6.3), gutter casts are present, whereas the finer grained facies (particularly silt-bearing clay-rich mudstones) contain individual units that are commonly organised into thin-beds with a normally graded "triplet" motif. The gutter casts here are oriented at right angles to the prevailing ripple directions and typically contain laminae that lap on to the scour margins (Greensmith et al. (1980) summarise the distribution of these and related structures in the Cleveland Ironstone Formation). The gutter casts are likely to have been deposited in association with storm set-up in relatively proximal settings (Whitaker, 1973; Greensmith et al., 1980; Rawson et al., 1983; Macquaker and Taylor, 1996) or are the products of geostrophic currents (e.g. Plint and Walker, 1987; Myrow, 1992; Philip et al., 2003; Varban and Plint, 2008).

In contrast, the depositional processes responsible for the normally graded "triplet" motif observed in the more distal facies are only poorly known. The motif appears superficially similar to muddy turbidites (e.g. Stow and Bowen, 1980; Alexander and Morris, 1994). However, they are subtly different to classical turbidites because they exhibit an abrupt internal transition between a basal, largely homogenous silt-rich laminaset with concave up ripple foresets to the overlying intercalated continuous parallel silt and clay-rich laminae before being overlain by a clay drape. These triplet structures are remarkably similar to the microfabrics interpreted as the products of wave enhanced, sediment gravity flows (WESGFs) of fluid mud (Macquaker et al., 2010a). In WESGFs wave activity and gravity combine to generate downslope directed currents across shelves with very low slopes (e.g.

Friedrichs and Wright, 2004; Traykovski et al., 2007). These recently recognised dispersal process are responsible on modern shelves for significant offshore-directed sediment transport over very low gradients (<0.5°) that are too low for classical turbidites to be initiated and sustained by autosuspension processes (e.g. Pantin, 1979; Swift, 1985; Nittrouer and Wright, 1994; Wright et al., 2001). Wignall et al., (2005) noted that hummocky cross stratification (HCS) was present close to the top of the Grey Shales. The fabrics they illustrated (their Figure 4) are very similar to those interpreted here as being products of WESGF's. Given that HCS is rarely developed in mudstones and typically has much longer wavelengths, we prefer a wave-modified density flow interpretation for these structures. Of course, both types of feature are formed during storms by the effects of waves, so detailed interpretation of their formative process makes little difference to the overall interpretation that storm-driven combined flows were operating at the sea floor to disperse sediment in this basin.

The presence of triplet beds and diminutive ripples, even in the anoxic basinal parts of the succession, indicates that advective sediment transport either via wave enhanced density flows or by traction currents played at least some role in delivering and dispersing sediment throughout the studied succession. The abundance of these fabrics in the Mulgrave Shale Member (present in 10 of 30 samples in this unit) suggests that conditions in the bottom water layers of the water column were not as low energy as most previous researchers have argued and that there are direct linkages between process occurring updip and downdip in this succession.

6.6.2. Suspension settling

While most of the succession contains microfabric evidence indicating that advective sediment transport processes delivered a significant fraction of the sediment, the upper units (Mulgrave Shale Member) contain some textural fabrics which suggest that suspension settling was also a sediment delivery process. In the clay-, calcareous nannoplankton-, organic carbon-bearing mudstones of this interval, much higher proportions of material with a production origin, particularly organic-carbon, coccoliths and foraminifera are present. Detailed textural analyses of these biologically derived materials reveal that much of the organic matter is wispy and intimately associated with mineral matter (Figure 6.6). Moreover, a high proportion of the tests occur within faecal pellets that are enclosed by envelopes of clay minerals and organic matter. Together these materials appear to be bundled into aggregates composed of both organic and inorganic materials that are held together by extracellular polysaccharides (cf. Macquaker et al., 2010b). These organo-minerallic aggregates are very common in recent marine settings (e.g. Alldredge and Silver, 1988; Alldredge and Gotschalk, 1990) and form “marine snow” when larger than 0.5 mm in diameter. In modern oceans the majority of the sediment reaching the sediment water interface does so either as flocs, particularly where there are changes in salinity, as faecal pellets that result from the feeding strategies of herbivores and zooplankton in the surface water layers, or from random collisions between particles (e.g. McCave, 1984, 2005). Crucially, these aggregate grains have settling rates orders of magnitude greater than individual grains, causing organic matter to be delivered to the sediment-water interface rapidly (Macquaker et al., 2010b). In modern oceans, abundant marine snow formation is particularly associated with zones of high primary production resulting from nutrient inputs to the photic zone.

6.6.3. Bioturbation

Bioturbation intensity on continental shelves is controlled by sediment accumulation rates and reoccurrence frequency of sediment delivery events, bioavailability of oxidants and reductants, and substrate composition (e.g. Bentley et al., 2006). In the studied succession there is plentiful detailed petrographic evidence that burrowing activities disrupted the sediment and were responsible for obliterating many of their depositional fabrics. In the Cleveland Ironstone Formation and Grey Shales Member, most of the primary sediment fabrics, particularly in the finer-grained mudstone lithofacies (e.g. clay-rich mudstones) were disrupted by diminutive burrows such as *Chondrites isp*., *Phycosiphon isp*., *Rhizocorallium isp.* and *Planolites isp*. (Figure 6.5). The presence of such bioturbation indicates that the reoccurrence frequency of storm events varied and during intervening fair-weather periods there was sufficient time for complete colonization of most beds (e.g. Bromley, 1990; Ekdale and Bromley, 1991; Goldring et al., 1991; Bentley et al., 2006). Where laminae are preserved, particularly in the silt-bearing, clay-rich mudstones (Figure 6.4), it is likely that there was insufficient time between storm episodes for the sediment to be completely homogenised prior to the next sedimentation event. Thus the sedimentation rates were more rapid in lithofacies with original sedimentary structures preserved than in lithofacies where the original structures have been completely destroyed. This pattern, however, changes markedly in the Mulgrave Shale Member where a much greater proportion of the original depositional fabrics within individual beds are preserved. However, there is still evidence that a diminutive infauna were able to colonise the sediment (producing *Phycosiphon isp*. and *Planolites isp*.) and that a mixed layer had formed in the surficial sediment layers at the sediment water interface (cf. Macquaker et al., 2010b). While the bottom water layers were likely dysoxic, the abundance of thin beds with homogenized tops in this part of the succession suggests that long-term persistent bottom water anoxia cannot have been a feature of this basin.

6.7. Conclusions

Combined hand-specimen, optical, electron-optical and geochemical analyses reveal a wide range of lithofacies variability in the Lower Jurassic succession of the Cleveland Basin, North Yorkshire Coast, England. Detailed analyses of 151 samples has enabled six lithofacies to be identified: (1) sand- and clay-bearing, silt-rich mudstones, (2) silt-bearing clay-rich mudstones, (3) clay-rich mudstones, (4) clay-, calcareous nannoplankton-, organic carbon-bearing mudstones, (5) fine-grained muddy sandstones, and (6) cement-rich mudstones.

Systematic variations in grain size and abundance of production-derived materials indicate that during deposition there was a change in the balance of primary production relative to dilution and length of the detrital sediment transport path. Units with higher sand and silt components were deposited in relatively proximal settings, whereas units that are more clay-rich and comprise a greater proportion of production-derived materials were deposited in more distal areas.

Microtextural analysis reveals that episodic advective sediment transport events likely driven by the presence of storm-generated waves and currents supplied a significant proportion of the sediment throughout the studied interval. The textures present (sharp-based and normally graded “triplet” beds, ripples, gutter casts) indicate that at least some material was supplied to the basin by conventional storm mixing to produce normally graded “tempestites”, while elsewhere sediment was dispersed by wave-enhanced sediment gravity flows of fluid mud and by turbulent flows that generated ripples. The presence of these structures in distal deposits indicates that the processes responsible for deposition here were not just driven by suspension settling processes in spite of the fact that there is good evidence that the water column developed anoxia. Moreover, the presence of burrows at the tops of many beds suggests that the reoccurrence frequency between storm events sufficiently long to allow at least some sediment colonisation between storm events. Crucially, the existence of bioturbation in many of the finest grained units, even in the Mulgrave Shale Member, also indicates that long-term and persistent bottom water anoxia during deposition of this succession is unlikely to have existed although short-term anoxia is highly likely.

In the more distal part of the succession, suspension settling supplied additional sediment to that being deposited by bedload and density currents. Detailed textural analyses reveal that much of the sediment with an organic origin was delivered to the sediment water interface as faecal pellets, flocs or other aggregates composed of both organic and inorganic materials. These organo-minerallic aggregates are common in modern marine settings as marine snow.

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Chapter 7

Sedimentological controls on the preservation of organic carbon in fine-grained sediments and the "Goldilocks Condition": a case study of the Grey Shale and Mulgrave Shale (Toarcian, Lower Jurassic) preserved in northeast England

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7.1. Abstract

Persistent bottom water anoxia, coupled with predominantly low energy conditions at the sediment / water interface, are commonly argued to play substantive roles in the enhanced preservation of organic carbon in ancient fine-grained sedimentary rocks. Presence of bioturbation and evidence of physical sediment reworking in some organic carbon-rich units, however, suggests that the physical and chemical processes that occur while organic carbon is being preferentially preserved are only poorly understood, and in particular the requirement for bottom water anoxia in this process may have been overestimated. To examine how the physical and chemical processes interact to enhance organic carbon preservation in fine-grained sedimentary successions, the Whitby Mudstone Formation (Grey Shale and Mulgrave Shale Members) has been investigated using combined systematic field logging, detailed microtextural investigation of 90 unusually thin polished thin sections and whole rock geochemical techniques.

The analyses reveal that four thin-bedded mudstones can be recognized. These include: (a) silt-bearing, clay-rich mudstones; (b) clay-rich mudstones; (c) clay-, calcareous nannoplankton-, organic carbon-bearing mudstones; and (d) cement-rich mudstones. Most, with the exception of the carbonate cement rich mudstones are predominantly composed of detrital clay-sized material and silt-sized quartz, in addition to calcareous microfossils (coccoliths and foraminifer), diagenetic pyrite and up to 14.2% TOC (in the Mulgrave Shale Member). Many of the samples also contain evidence of having been colonized by a diminutive infauna. Where depositional fabrics are preserved, however, normally-graded beds, silt lags, micro-scours, ripples, parallel lamination, shell pavements and discontinuous, pelleted wavy-laminae are present. In addition, much of the organic matter present is intimately associated with the mineral matrix and is organised into organo-minerallic / pellet rich aggregates. These aggregates are particularly common in the basal laminae of the thin-bedded and pelleted, clay-, calcareous nannoplankton- and organic carbon-bearing mudstones.

These micro-textures suggest that the sediment was delivered to the sites of deposition by both advective, sediment transport processes operating close to the sediment water interface and by suspension settling as marine snow aggregates and pellets. The presence of these fabrics suggests that sedimentation was dominated by event beds and particularly

where organo-minerallic aggregates are present organic carbon was delivered rapidly to the sea floor as large composite grains rather than as a rain of fine-grained detritus. Rapid delivery and burial meant that organic carbon had the maximum chance of being preserved. Top-down colonization of individual beds indicates that between sediment delivery events, a restricted infauna was able to colonize the sediment. These microfabrics indicate that during deposition of the Whitby Mudstone Formation the bottom waters, while they may have been dysoxic, were not persistently anoxic and that enhanced organic matter preservation in this interval was a function of high primary organic production and limited access to oxidants because the reoccurrence frequency of individual beds events was more rapid than the rates of sediment colonization. Here the existence of bottom water anoxia was likely a byproduct of high rates of organic matter decay in the bottom water layers rather than a pre-requisite for enhanced organic carbon preservation.

7.2. Introduction

Source rocks (sedimentary rocks that contain > 2% total organic carbon (TOC) (after Tissot and Welte, 1989) are commonly interpreted as being the products of deposition in low energy, anoxic / dysoxic basins where the rates of organic carbon production in the water column were relatively high and sediment accumulation rates were optimised to minimise dilution and maximise organic carbon preservation (e.g. Tyson, 1995, 2001, 2005; Bohacs, 1998; Bohacs et al., 2005; Katz, 2005). These conclusions arise mainly from their physical appearance in hand specimen (specifically their fine grain sizes, lack of obvious tractional sedimentary structures, preservation of laminae and reduced infauna) and their geochemical characteristics, (specifically their elevated total organic carbon contents, common occurrence of biomarkers indicative of water column photic zone anoxia (e.g. Kenig et al., 2004; Van Dongen et al., 2006), elevated concentrations of redox sensitive metals (e.g. Dean and Gardner, 1982; Arthur et al., 1987; Arthur and Dean, 1998; Algeo, 2004), and their small framboid sizes (e.g. Wilkin et al., 1996; Wilkin and Barnes, 1997; Wignall et al., 2005)). These physical and chemical attributes have led researchers to conclude that physical vertical water column circulation was restricted commonly by the presence of some form of sill at the basin entrance (e.g. Morris, 1979; Demaison and Moore, 1980; Sælen et al., 1996; Otis and Schneidermann, 1997; Sælen et al., 2000; Rohl et al., 2001; Frimmel et al., 2004; Rohl and Schmid-Rohl, 2005; Loucks and Ruppel, 2007), essential nutrients to fuel primary production in the photic zone were readily available and derived mainly from upwelling (e.g. Cook and McElhinney, 1979; Pedersen and Calvert, 1990; Hay, 1995; Parrish, 1995; Tribovillard et al., 1996), and more or less persistent bottom water anoxia / dysoxia was developed in the basin centres (e.g. Wignall, 1991; Sælen et al., 2000; Wignall et al., 2005; McArthur et al., 2008; Caswell et al., 2009). Recently, researchers have noted that optimising sediment accumulation rates in order to bury organic matter efficiently, is also very important (e.g. Coleman et al., 1979; Demaison et al., 1984; Macquaker and Gawthorpe, 1993; Stow et al., 2001; Tyson, 2001; Bohacs et al., 2005).

While many studies implicitly recognise that there are a variety of potential pathways, that might create the necessary conditions to preserve organic matter (e.g. Bohacs et al., 2005), most researchers argue that during source rock deposition the fine-grained sediments, were delivered to the site of deposition as a continuous, dispersed rain of sediment settling out from buoyant blooms via suspension settling. Indeed, vertical water column stability is commonly cited (e.g. Tyson and Pearson, 1991; Tyson, 1995) as being the most important single factor in determining and controlling both benthic oxygen levels and productivity of mid-latitude shelf plankton.

The recent application of petrographic techniques (scanning, optical, and electron optical methods) applied to fine grained successions generates microtextural data (e.g. Macquaker and Keller, 2005; Macquaker et al., 2007) provides significant insights into the processes responsible for fine-grained sediment production, its dispersal, and subsequent burial. For instance, these methods show that advective transport processes operating both at and close to the seafloor, as evidenced by the presence of ripples, gutter casts and wave-enhanced gravity sediment gravity flows of fluid mud, were all likely operating at the time of deposition and responsible for some of the sediment dispersal (e.g. Macquaker and Bohacs, 2007; Schieber et al., 2007; Schieber and Southard, 2009; Macquaker et al., 2010a; Ghadeer and Macquaker, 2011). These microfabric data, suggests that in these basins the mechanisms that underpin source rock formation are likely much more complicated than most researchers have suggested. This increased complexity arises because, in addition to considerations of the inter-related roles of bottom water anoxia, enhanced primary production and optimizing overall rates of sediment accumulation; it is now also necessary to consider the possibility that sediment was not just being delivered by suspension settling but also by high energy events that were operating to erode and transport sediment laterally at the sediment water interface.

7.3. Aims and objectives

In the light of these comments the main aims of this study are to investigate the microfabrics present in a mudstone succession that includes intervals that have both average, and elevated organic carbon contents, and where persistent bottom water anoxia has been proposed as a significant factor controlling facies variability. With these data it will be possible to identify the main physical mechanisms responsible for sediment dispersal, delivery and subsequent reworking while organic-carbon was being preferentially preserved and a source rock was being formed.

The mudstone-dominated succession, which includes the Lower Jurassic Grey Shale and Mulgrave Shale Members of the Whitby Mudstone Formation exposed in the Cleveland Basin (Figure 7.1) in North Yorkshire (UK), is an ideal natural laboratory for this study. It meets these criteria because the succession is well-exposed and contains both organic carbon-rich (Mulgrave Shale Member) and organic carbon lean intervals (Grey Shales Member). In addition, this succession has been extensively studied as part of investigations into the origin of the Toarcian anoxic event (e.g. Jenkyns, 1988; Hesselbo and Jenkyns, 1995; Sælen et al., 1996; Kemp et al., 2005; Wignall et al., 2005; Cohen et al., 2007) and into the formation of pyrite (e.g. Raiswell and Berner, 1985; Newton, 2001; Wignall et al., 2005). Finally, detailed stratigraphies of this succession are also available (e.g. Howarth, 1973; Powell, 1984, 2010; Pye and Krinsley, 1986; Rawson and Wright, 1992, 1996) and form the basis of the stratigraphy used here.

In order to meet these aims the: a) background geology of the studied succession is reviewed, b) methods used to describe the mudstone lithofacies present are described, c) key fabrics and other compositional attributes of the lithofacies present are presented and d) the implications of these data in the context of the fundamental mechanisms associated with the preservation of organic matter and the origin of this source rock is discussed.

7.4. Geological setting

Lower Jurassic aged mudstones present in the Cleveland Basin are similar to many other fine-grained siliciclastic mudstone dominated successions deposited across North West Europe at this time. The succession at Port Mulgrave contains classic examples of oil-prone sources rock e.g. the Mulgrave Shale Member (Jet Rock), which is the lateral equivalent of the Posidonia shale in northern Europe where it contains up to 16% TOC (e.g. Leythaeuser et al., 1988; Schaefer and Littke, 1988; Savrda and Bottjer, 1989; Littke et al., 1991; Prauss et al., 1991; Radke et al., 2001; Rohl et al., 2001; Schmid-Rohl and Rohl, 2003; Schwark and Frimmel, 2004; Rohl and Schmid-Rohl, 2005; Munoz et al., 2007). These mudstones contain significant quantities of organic carbon derived from marine algal and bacterial components and many researchers (e.g. Wignall and Hallam, 1991; Ibrahim, 1995; Sælen et al., 1995; Sælen et al., 2000; Kemp et al., 2005; Wignall et al., 2005) have concluded that they were likely deposited in outer shelf to basinal environments.

The 13 m thick Gray Shale Member forms the lower part of the Whitby Mudstone Formation. Most researchers (e.g. Rawson and Wright, 1992, 1996, 2000; Sælen et al., 1996; Sælen et al., 2000; Wignall et al., 2005) describe it as being composed of bioturbated (Bioturbation Index 5, see Wignall et al., 2005) pale- to dark-grey mudstones with subordinate strata that contain concretionary siderite and calcite cements. In some intervals, where the sediment has not been homogenised, wave enhanced sediment gravity flows of fluid mud, and ripple lamination have been recorded (Ghadeer and Macquaker, 2011). Locally (at Kettleness a few kilometres to the east of Port Mulgrave), Wignall et al. (2005) reported the presence of hummocky cross stratification towards the top of this unit. A relatively diverse fossil assemblage has also been found in the Grey Shales including *Protocardia* sp., *Eotrapezium* sp., and *Nuculana* sp. as well as ammonites, belemnites and fragments of wood (e.g. Sælen et al., 1996; Wignall et al., 2005; Caswell et al., 2009). Some of this fossil material is organised into thin shell pavements that mainly comprise compacted and disarticulated bivalves. The organic carbon within the Grey Shale Member exhibits relatively low hydrogen indices (average 250) (see Sælen et al., 2000; Wignall et al., 2005) and large pyrite framboid sizes (average 5 µm, range approximately 3 µm to 9 µm) in comparison to the overlying Mulgrave Shale Member (see below).

Most authors (e.g. Sælen et al., 1996; Sælen et al., 2000; Wignall et al., 2005; Hesselbo et al., 2007; Caswell et al., 2009; Powell, 2010) have concluded that the Grey Shale Member was mostly deposited by suspension settling under fully marine conditions where the sediment pore waters varied from being oxic to dysoxic. The recent recognition, however, that this unit contains diminutive ripples, wave enhanced sediment gravity flows of fluid mud and hummocky cross stratification suggests that conditions at the sediment water interface were likely rather more energetic than earlier researchers had noted (e.g. Wignall et al., 2005; Ghadeer and Macquaker, 2011).

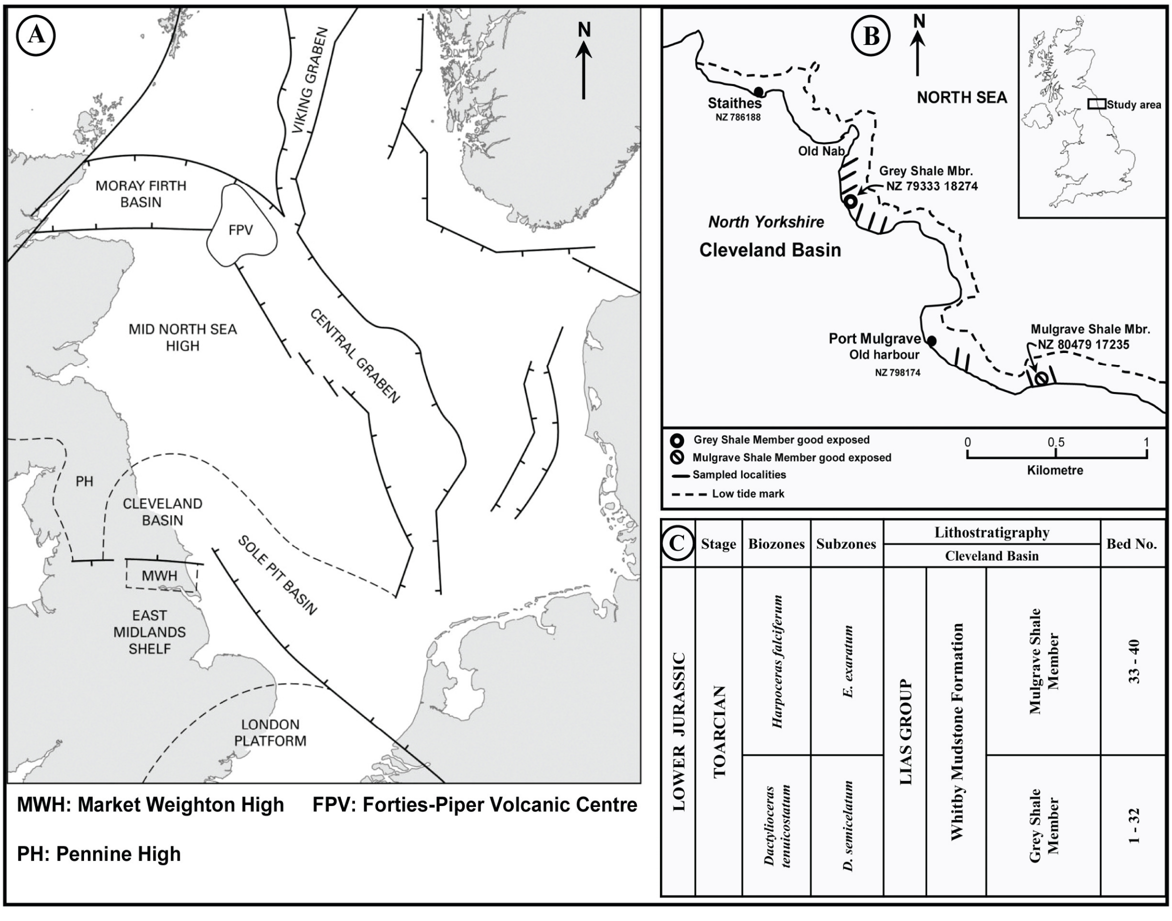

Figure 7.1. A) Generalised palaeogeographical map during the Jurassic showing the Cleveland Basin and the NE England coastline. From Powell (2010) after Knox et al. (1991). B) Location map showing the study area in the Cleveland Basin, North Yorkshire Coast (England) where the Grey Shale Member and Jet Rock Member are good exposed, and the localities were samples collected at. C) Stratigraphic context of the studied interval (after Knox, 1984; Powell, 1984; Rawson and Wright, 2000).

The facies and benthos dramatically changes in character at the top of the Grey Shale Member and into the base of the Mulgrave Shale Member. Here low diversity high abundance infauna (Bioturbation Index 1) on specific bedding planes becomes dominant (mainly *Pseudomytiloides* sp.) and the strata become noticeably darker with preserved partings being visible in the sediment (e.g. Rawson and Wright, 1996, 2000; Wignall et al., 2005; Caswell et al., 2009).

The upper unit of the Whitby Mudstone Formation is the Mulgrave Shale Member (8 m thick). These strata are typically described, on the basis of their appearance in hand specimen, as comprising laminated, sulphur- and organic carbon-rich "bituminous shales" that contain thick bands of calcareous concretions, and rare shell pavements (e.g. Myers and Wignall, 1987; Rawson and Wright, 1996). The organic matter in the Mulgrave Shale Member exhibits high hydrogen indices that range from 500 to 750 (e.g. Sælen et al., 1995; Sælen et al., 1996), and at some levels unusually low bulk $\delta^{13}C$ isotopic values relative to other organic carbon-rich mudstones (e.g. Jenkyns and Clayton, 1997; Kemp et al., 2005). These attributes have been linked to the coincidence in this interval of both mass extinction and oceanic anoxic events (e.g. Jenkyns and Clayton, 1997; Sælen et al., 1998; Kemp et al., 2005; Wignall et al., 2005; Kemp et al., 2006; Cohen et al., 2007). Detailed petrographic and geochemical analyses of these units reveal that pyrite framboid diameters are small (average 3 µm, range from 2 µm to 5 µm) and degrees of pyritization (DOP) exceed 0.75 (Newton, 2001). Recent petrographic analyses have also revealed that the strata in the Mulgrave Shale are organised into very thin beds that exhibit scoured bases (<5 mm thick), compacted ripple laminae, wave enhanced sediment gravity flows of fluid mud and organo-minerallic aggregate microfabrics (Ghadeer and Macquaker, 2011).

From these data most authors have concluded that the mudstones of the Mulgrave Shale Member were mainly deposited from "background" suspension settling in a basinal setting, where the bottom water layers were predominantly anoxic / euxinic (e.g. Pye and Krinsley, 1986; Wignall, 1991; Sælen et al., 1995; Rawson and Wright, 1996; Sælen et al., 1996; Jenkyns and Clayton, 1997; Kemp et al., 2005; Wignall et al., 2005; McArthur et al., 2008). These researchers have typically concluded that during sediment deposition high primary production coupled with persistent bottom water anoxia were responsible for the significant organic carbon preservation in this prolific source rock interval. The presence of rare shell pavements, however, indicates that the bottom waters were occasional disrupted by oxygenation events that allowed brief periods of benthic colonization (e.g. Fursich and Oschmann, 1986; Rohl et al., 2001; Rohl and Schmid-Rohl, 2005). The abundance of pyrite in these units, particularly where pyrite framboid sizes are very small

(<5 μm) also indicates that both in the water column and shortly after deposition the waters were anoxic and sulfidic (e.g. Raiswell, 1982, 1993; Wignall and Newton, 1998). The existence of very thin compacted ripples and beds that exhibit "triplet" structures in these basinal mudstones, however, suggests that conditions at the sediment / water interface were at least occasionally being reworked by physical processes operating to transport deposit sediment over the seabed (Ghadeer and Macquaker, 2011).

7.5. Material and methods

In order to collect the necessary data to make the detailed lithofacies descriptions to investigate the physical processes operating at the time of deposition unusually thin (0.02 to 0.025 mm), polished, and large (c. 40 x 60 mm) thin sections were prepared from 90 samples collected at 0.25 m intervals through the Grey Shale and Mulgrave Shale Members of the Whitby Mudstone Formation (Figure 7.2). Initially, each thin section was scanned in a flat bed 35 mm film scanner (Epson Perfection 3170) to obtain details of 10^{-2} to 10^{-3} m-scale textures present. Once these data had been obtained, the thin sections were analysed using a petrographic microscope (Nikon Labophot) to obtain textural, compositional and diagenetic data at the scale of 10^{-3} to 10^{-4} m. Finally, to obtain details of 10^{-4} to 10^{-5} m-scale textural and mineralogical variability, each thin section was investigated electron-optically using a JEOL 6400 scanning electron microscope (SEM) equipped with a Link 4-Quadrant, backscattered electron (BSE) detector, semi-quantitative, X-ray spectrometer, and energy dispersive (ED) analytical system. The SEM was operated at 20 kV and 2.0 nA, with 15 mm working distance.

The mineralogy of each sample was obtained by x-ray diffraction (XRD) analyses. This was accomplished on a Bruker D8 Advance diffractometer, using Cu, K α1 radiation at 40 KV, 40 mA. Finally, the organic carbon contents of each sample were obtained by differential combustion in a Leco CS244 carbon analyser of untreated and acid-treated mudstones. Initial calibration was made using Leco standard carbon steel rings (1g, nominal carbon content 0.8%) and verified by analysis of a certified reference material.

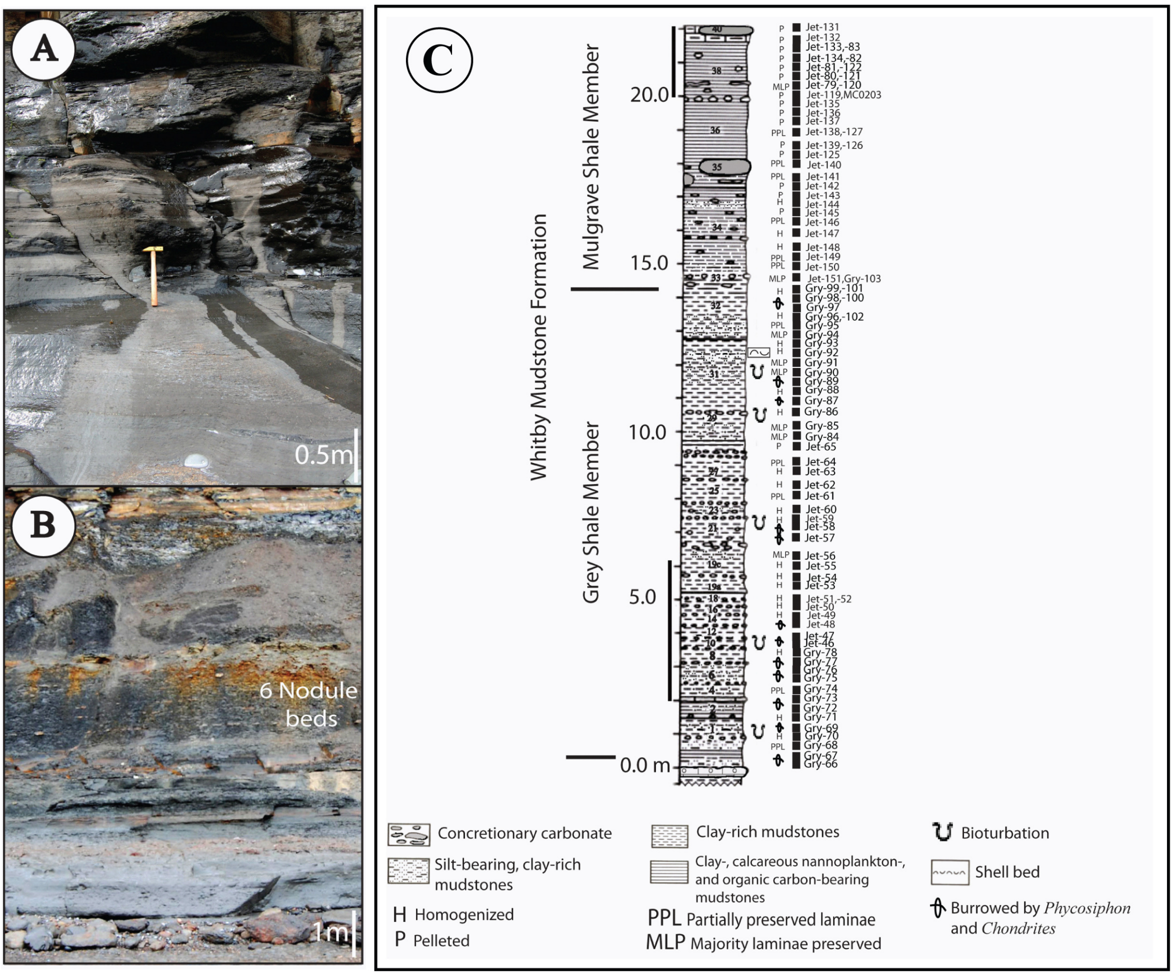

Figure 7.2. Field photographs and Logged intervals of the studied succession: A) Mulgrave Shale Member, Whitby Mudstone Formation; B) Grey Shale Member, Whitby Mudstone Formation; C) Details of logged and sampled succession of the Grey Shale Member and Mulgrave Shale Member (Whitby Mudstone Formation), showing bed numbers, sample locations, mudstone lithofacies, and lithofacies structures in each sample. Log modified after Howarth (1992); Rawson and Wright (1996). The bed numbers were obtained from Howarth (1973).

7.6. Results

Four mudstone lithofacies were recognized in the studied succession. The nomenclature used to describe these rocks is based on their microtextural attributes as well as their grain sizes and mineralogies. It is slightly modified from the scheme proposed by Macquaker and Adams (2003). The mudstone facies present include:

a) Thin-bedded silt-bearing, clay-rich mudstone;
b) Thin bedded clay-rich mudstone;

c) Thin-bedded and pelleted, clay-, calcareous nannoplankton-, and organic carbon-bearing mudstone; and
d) Cement-rich mudstones.

Of these four, only the first three are pertinent to this study and are described in detail below. The stratigraphic distributions of these facies is summarised (Figure 7.2).

7.6.1. Silt-bearing, clay-rich mudstone

This lithofacies was encountered in 15 samples within the Grey Shale Member of the Whitby Mudstone Formation. In this part of the succession the silt-bearing, clay rich mudstones typically form stacked successions of thin, normally-graded beds (5 to 20 mm thick), which have scoured bases (mm-scale vertical relief) (Figure 7.3). Internally, while many of these individual beds preserve some primary lamination, their tops are commonly homogenized by the burrowing activities of a diminutive infauna (variously attributed to *Phycosiphon* isp., *Planolites* isp*.,* and *Chondrites* isp.). Where preserved the laminae exhibit a variety of geometries and have varying continuity across the individual sections. For instance, curved non-parallel, to parallel and wavy geometries are present and individual lamina are either continuous or discontinuous (Figure 7.3A, B). Some of the individual beds exhibit a "triplet motif" (present in 5 of 15 samples in this lithofacies, figure 7.3A). These triplets comprise a homogeneous basal sub-unit that exhibits faint concave-up ripple laminae that are largely composed of silt-sized grains. These basal coarse sub-units are abruptly overlain by intercalated parallel and wavy laminae composed of silt and clay-sized materials, before being capped by a sub-unit composed of homogenous clay. The basal laminae within these triplets may also contain small grains of reworked fragmentary shell debris derived from bivalves, ammonites, echinoderms, and planktonic foraminifers.

The framework component of these silt-bearing, clay-rich mudstones is composed mainly of silt-sized quartz, K-feldspar, detrital muscovite, calcareous material derived from the fragmented tests of organisms and woody carbonaceous debris. These framework materials are preserved in a matrix of clay-sized debris composed mainly of illite and mixed layer illite / smectite, some calcite (both as small cement masses and coccolith debris), kaolinite, amorphous organic matter, both framboidal and euhedral pyrite and minor siderite (Figure

7.3C, D). The TOC content of these units averages 1.2% and ranges from 0.5 to 3.63%. Visual inspection reveals that the distribution of organic carbon varies significantly within individual beds. For instance, carbonaceous material is more abundant in the intercalated clay and silt-rich laminae and relatively depleted in the homogenous laminae (Figure 7.3C, D).

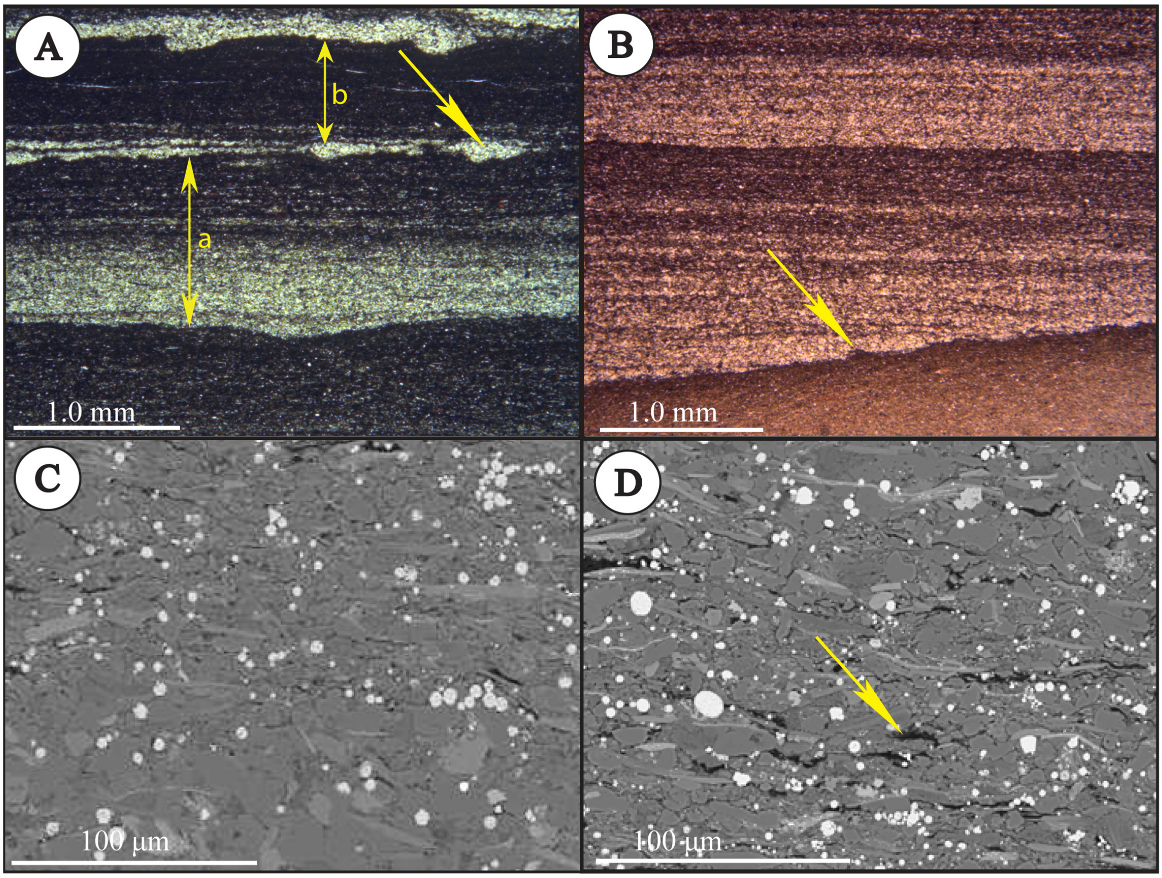

Figure 7.3. A) Plane-polarised light of a representative silt-bearing, clay-rich mudstone (Gry-90) showing stacked succession of thin beds that have erosional bases. Each individual bed shows a triplet motif structure (double side arrows beds a and b) commonly <10 mm thick containing basal silt-rich lamina, overlain by continuous intercalated silt and clay-rich lamina in their middle portions, and homogenized, clay-rich drape at their tops. Note the presence of silt lag at the bed bases (arrow). B) Low-power optical micrograph of the same facies (Gry-84) showing normally graded thin beds with some preserved internal laminae that onlap the basal erosional surface (arrow). C) High-power, backscattered electron-optical micrographs of the sample Gry-90 illustrating the distribution of organic matter close to the upper homogenized parts of the thin beds. Note that the organic matter forms small plate like grains in a matrix of clay-sized materials, some calcite, and pyrite (TOC: 1.95%). Also note the presence of silt-sized material composed of quartz, some feldspar, with minor muscovite. D) High-power, backscattered electron-optical micrographs of Gry-84 collected from the laminated layer close to the bed base and illustrating silt sized material (mainly of quartz, some feldspar, and minor muscovite) in a matrix of clay-sized materials composed of kaolinite, illite, amorphous organic matter (arrow) with 2.05% TOC, some calcite, and pyrite.

7.6.2. Clay-rich mudstone

Clay-rich mudstones were encountered in 26 samples in the Grey Shale Member and 7 samples in the Mulgrave Shale Member. Individual units of this facies are typically organised into stacked successions of thin beds that form bedsets up to 0.2 m thick. The clay-rich mudstones encountered in the Grey Shale Member are typically completely homogenized while those in the Mulgrave Shale Member commonly preserve some lamination. Individual beds are typically thin (up to 10 mm thick), sharp-based and notwithstanding the overprinting effects of homogenization, normally-graded. The basal contacts of these beds are commonly defined by silt lags that are commonly just a few grains thick. These lags may also contain fragmentary bivalve, echinoid and planktonic debris (Figure 7.4A, B). Some of the clay-rich mudstone beds exhibit a triplet motif (present in 10 of 33 samples in this lithofacies, Figure 7.4B), which has similar attributes to those found in the silt-bearing clay-rich mudstones described above, albeit developed in finer grained lithofacies.

The matrix component of the clay-rich mudstones is mainly composed of clay-sized material minerals composed of illite, mixed layer illite-smectite, amorphous organic matter, kaolinite, small aggregates of calcite, and siderite as well as pyrite (both euhedral and framboidal). In contrast, the silt-sized framework component of these units is mainly composed of quartz, some K-feldspar, detrital muscovite, and calcareous biogenic debris (Figure 7.4C, D). The TOC content of this units averages 2.76% overall (range 0.67 to 8.69%). There are also significant stratigraphic differences in TOC contents of this lithofacies. For instance in the Grey Shale Member the organic carbon contents average 2.11% (range from 0.67 to 6.03%) while in the Mulgrave Shale Member they average 5.19% (range from 3.54 to 8.69%). Visually, organic matter is more abundant in the non-bioturbated lamina of the individual beds particularly in the Mulgrave Shale Member than in regions where the laminae have been homogenized (Figure 7.4C, D).

Figure 7.4. (see next page): A) Thin section scan of a representative thin-bedded clay-rich mudstone (Jet-151) illustrating stacked succession of thin beds with erosional bases (arrows). The individual beds are normal graded and organised into the triplet motif. B). Plane-polarised light of a representative thin-bedded, clay-rich mudstone (Jet-149) illustrating stacked succession of upward fining thin beds (arrows). Each individual bed shows a triplet motif structure (double side arrows beds a and b) commonly <10 mm thick containing sharp-based, basal silt-rich laminae, overlain by continuous intercalated silt and

clay-rich laminae in their middle portions, and homogenized, clay-rich drape at their tops. Note the presence of reworked fragmentary shell debris (derived from bivalve, echinoid, and planktonic debris) at the base of bed b. C) High-power, backscattered electron-optical micrographs of Jet-151 collected from the upper homogenized parts of the thin beds. This micrograph illustrates silt sized material (composed mainly of quartz, some feldspar, and minor muscovite) in a matrix of clay-sized materials composed of kaolinite, mixed layer illite / smectite, some calcite, amorphous organic matter (TOC: 3.54%), minor siderite, and pyrite. D) High-power, backscattered electron-optical micrographs of the sample Jet-149. This micrograph was obtained from closed to the bed base in the laminated layer and contains silt sized material (composed mainly of quartz, some feldspar, and minor muscovite) in a matrix of clay-sized material minerals composed of kaolinite, illite, mixed layer illite-smectite, amorphous organic matter (arrow), small aggregates of calcite, siderite as well as pyrite cements. Note that the sample is very rich in organic matter (TOC: 4.60%) and much of the organic matter is organised into large, flattened wispy aggregates.

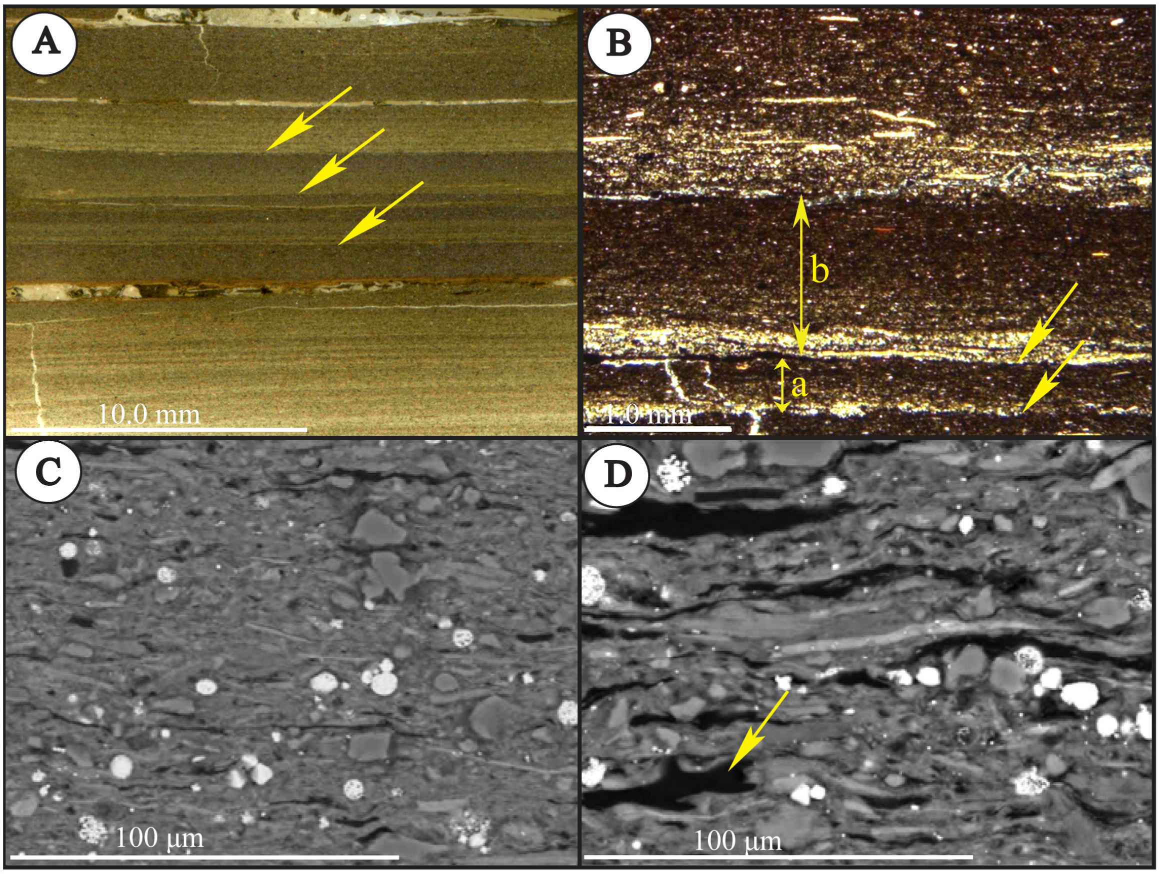

Figure 7.4. (see caption above)

7.6.3. Clay-, calcareous nannoplankton-, and organic carbon-bearing mudstones

This lithofacies was encountered in 28 samples of Mulgrave Shale Member and in 2 samples within the top part of the Grey Shale Member. In the field, it forms thin continuous brown to dark-grey coloured beds, which means that it can be readily distinguished from the other facies present.

Thin section analyses reveals that this mudstone type commonly forms stacked successions of very thin beds that form bedsets up to 0.2 m thick. The individual beds themselves are typically <5.0 mm thick. Internally, the individual beds are organised into wavy laminae that are either: (a) continuous and composed of flattened organo-minerallic aggregate-rich regions that mainly comprise amorphous organic carbon, pyrite and clay minerals and coccolith-rich faecal pellets (Figure 7.5), or (b) beds that comprise discontinuous laminae dominated by pelleted clay and organic debris at their bases and have homogenized clay-rich tops (Figure 7.7). Many of these beds exhibit sharp lower contacts and have very thin silt-lags (just a few grains thick) developed at their bases (Figure 7.6).

The framework component of the clay-, calcareous nannoplankton-, and organic carbon-bearing mudstones predominantly comprise silt-sized materials. The coarser components are mainly composed of quartz, with some phosphate, K-feldspar, and muscovite grains (Figure 7.7C, D). These framework components float in a clay sized-rich matrix that is composed of illite, mixed layer illite smectite, with some kaolinite and amorphous organic matter (TOC average 6.23%, range 3.25 to 14.2%). In addition, calcite, dolomite, minor siderite, and pyrite (mostly framboids) cements (see for example Figures 7.5C, D and 7.7C, D) may all be present. Where present the cement component occurs either as dispersed euhedra (<10 µm in size) or forms small < 100 µm microconcretionary masses.

Figure 7.5. (see next page): A) Thin section scan of a representative thin-bedded and pelleted clay-, calcareous nannoplankton-, organic carbon-bearing mudstones (Jet-122). This sample contains a stacked succession of thin beds that are each less than 3 mm thick. Each bed contains a very thin silt-lag at its base (arrows). Note the presence of bivalve shell fragment (SF) at the sample base. B) Low-power plane polarized light optical micrograph of the same sample (Jet-122), illustrating details of fragmentary shell debris (arrows) concentrated at the bed bases. In these beds the basal laminae are overlain by flattened organo-minerallic aggregates composed of organic carbon and coccolith-rich faecal pellets (arrowed P). C) High-power, backscattered electron-optical micrograph from Jet-122. The differing backscattered coefficients, coupled with the XRD data indicate that the silt sized material composed of quartz, minor K-feldspar, and detrital muscovite in a matrix that is predominantly composed of clay minerals that are mainly composed of kaolinite, illite, mixed layer illite smectite, and coccoliths in addition to pyrite, dolomite and siderite cemetns. Note much of the coccolith material is organised into pellets (arrow). The sample is very rich in organic matter (TOC: 7.86%). D) High-power, backscattered

electron-optical micrograph of the same sample Jet-122 illustrating large coccolith-rich faecal pellet (arrowed in C) partially enclosed by an organic carbon sheath.

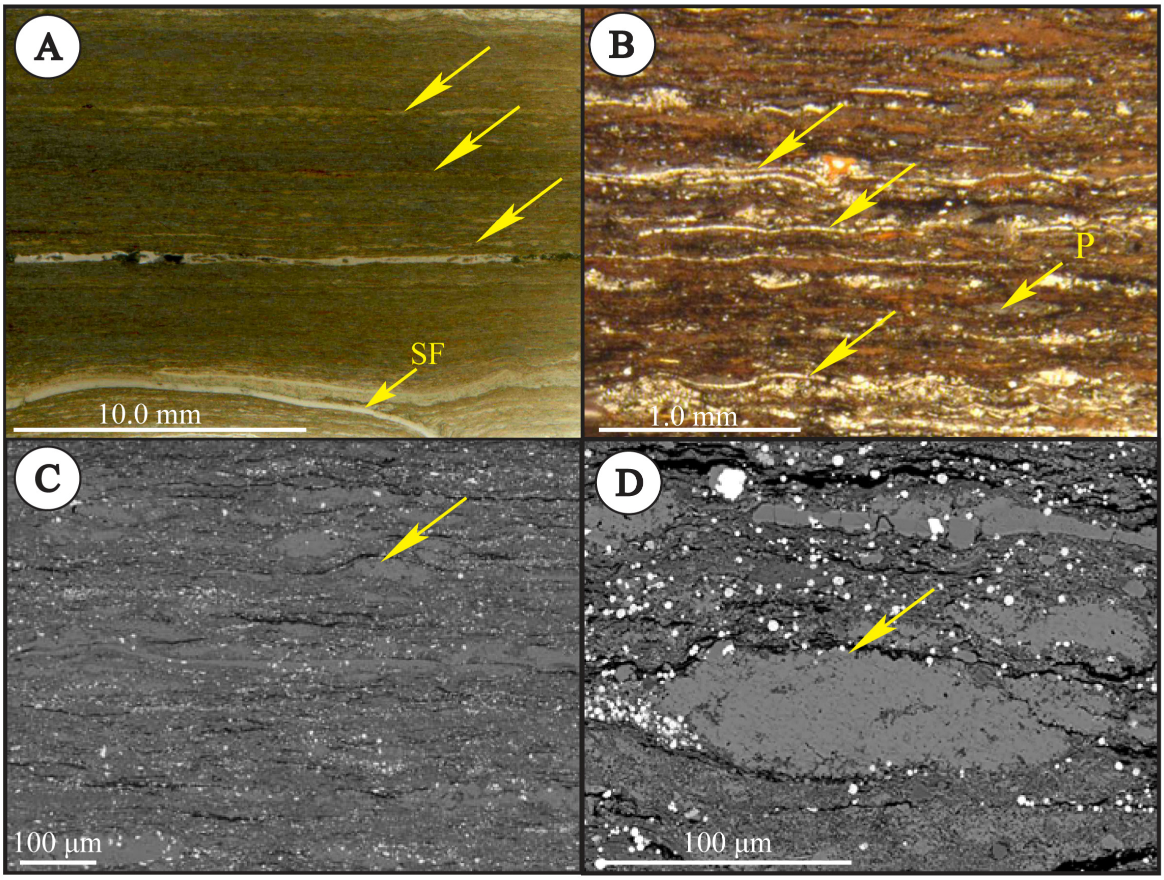

Figure 7.5. (see caption in previous page)

7.7. Discussion

7.7.1. Sediment dispersal in the Whitby Mudstone Formation: background to preserving organic carbon

Remarkable microtextural variability is preserved throughout this succession at <10^{-2} m scales. The abundance of normally-graded beds, with sharp / scoured bases, wave ripple laminae, hummocky cross stratification and "triplet fabrics" (see also Wignall et al., 2005; Ghadeer and Macquaker, 2011), indicates that throughout deposition of this succession the sediment was commonly being reworked (e.g. Aigner, 1982, 1985; Aigner and Reineck, 1982; Schieber, 1990; Swift and Thorne, 1991) and dispersed by storm-induced combined flows (e.g. turbulent flows producing wave ripples and wave-enhanced sediment gravity flows of fluid mud that produced the beds with the triplet motif (see also Myrow and

Southard, 1991; Myrow, 1992; Nittrouer and Wright, 1994; Plint et al., 2009; Macquaker et al., 2010a)). While the existence of these fabrics in the Grey Shale Member is not particularly remarkable, given its stratigraphic position overlying the Cleveland Ironstone Formation where similar fabrics are well-documented (e.g. Greensmith et al., 1980; Rawson and Wright, 1992, 1996; Macquaker and Taylor, 1996, 1997; Wignall et al., 2005; Macquaker et al., 2010a; Ghadeer and Macquaker, 2011) their existence in the Mulgrave Shale Member is more unexpected. This arises because most researchers (e.g. Rawson and Wright, 1996, 2000; Sælen et al., 1996; Jenkyns and Clayton, 1997; Sælen et al., 2000; Kemp et al., 2005; Wignall et al., 2005; Powell, 2010) have concluded that these organic carbon-rich (with up to 15% TOC) mudstones, were deposited in low energy environments by suspension settling (background sedimentation) out of buoyant plumes. The presence of stacked-beds in which the effects of erosion and the presence of ripples / triplet microtextures are so common indicates that during the deposition of the Mulgrave Shale Member the seafloor was being regularly reworked by storms and the sediment was not just being delivered by low-energy suspension settling mechanisms out of buoyant plumes but also be advective processes operating to disperse the sediment at and close to the sea floor. The existing sedimentological models that discuss how the unusual volumes of organic carbon were preserved during deposition of this unit, which mainly consider the role of suspension settling, must therefore be modified to take these microtextural observations into account.

In the Whitby Mudstone Formation, particularly in the beds composed of clay-rich mudstones (with TOC contents in the Grey Shale Member averaging 2.11% and in the Mulgrave Shale Member where they average 5.19%) and silt-bearing clay rich mudstones (TOC content in the Grey Shale Member averaging 1.2%), which also contain evidence of storm event beds and benthic colonization, it is likely that organic carbon preservation was linked explicitly to rapid and episodic deposition coupled with the effects of clastic dilution. During deposition of the event beds, organic carbon was rapidly buried and the only oxidants available to fuel its mineralization were buried with the sediment (either dissolved in the pore waters or as mineral oxidants), which led to organic carbon being initially preferentially preserved due to the restricted availability of oxidants. During the calm period, prior to deposition of the next event bed, benthic organisms were able to colonize the sediment from the sediment-surface down. This colonization led to the

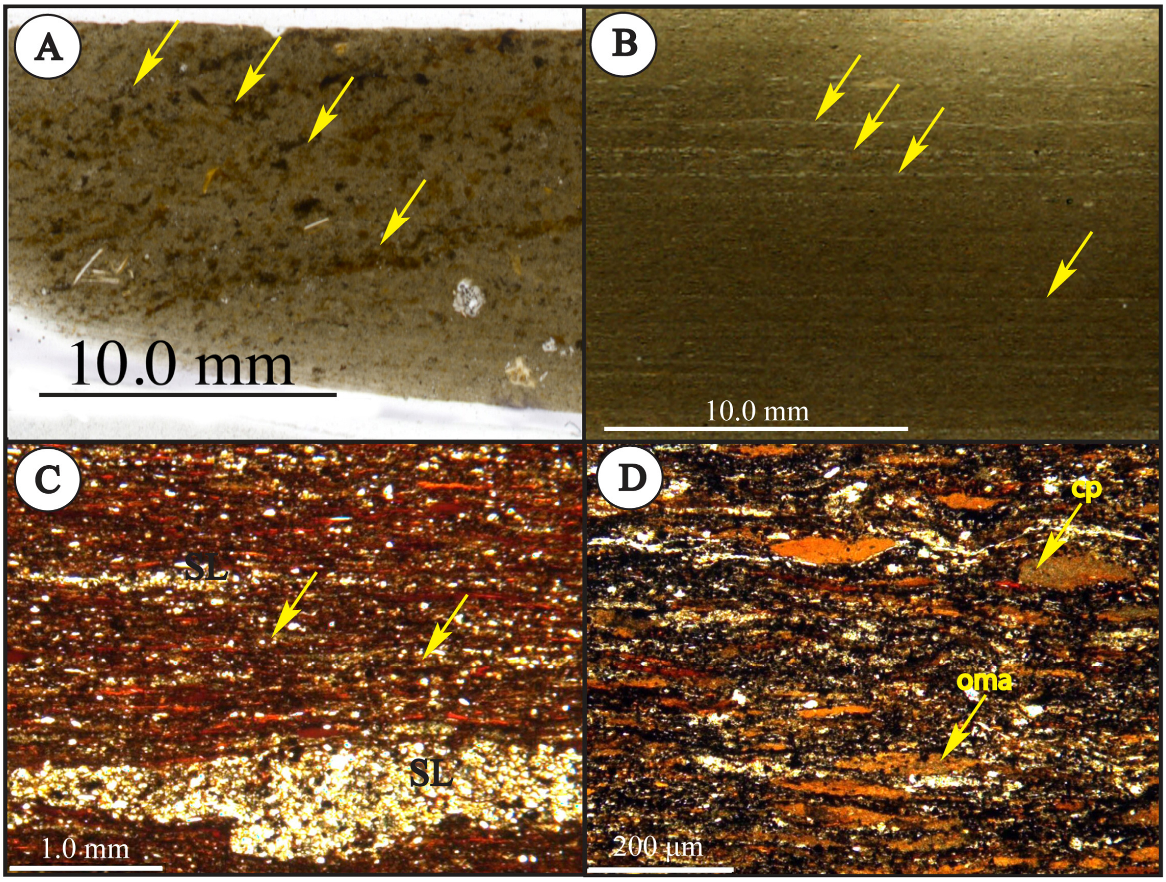

Figure 7.6. A) Thin section scan of a representative thin-bedded and pelleted clay-, calcareous nannoplankton-, organic carbon-bearing mudstones. This image was taken from a thin section made slight oblique to bedding (Jet-127). Note how the organic matter (TOC: 3.63%) is organised into relatively large grains up to 500 µm in diameter and particularly concentrated into the lamina at the base of the individual beds (arrows). B) Conventional thin section scan prepared in a bedding normal direction. The micrograph illustrates a stacked succession of thin-bedded and pelleted clay-, calcareous nannoplankton-, and organic carbon-bearing mudstones (Jet-132). Note that each bed has an erosional base (arrows). The sample is very rich in organic matter (TOC: 5.98%). C) Low to intermediate-power plane polarised light (PPL) of sample Jet-139. The basal contact illustrated here is erosional and overlain by thin, discontinuous silt-lags (SL). Overlying the basal lamina set are units enriched in clay and compacted organo-minerallic aggregates (arrows). D) Plane polarised light micrograph (Jet-139) illustrating, algal bodies flattened organo-minerallic aggregates (arrowed oma) and organic carbon and coccolith-rich faecal pellets (arrowed cp). The sample also is very rich in organic matter (TOC: 11.24%).

organic carbon being oxidized both because it was a reductant for the respiratory activities of the organisms as oxidants (e.g. oxygen and sulphate) were available, and because the pore waters were being irrigated which fuelled further microbial oxidation of the organic matter. As the oxidant front migrated downward through the sediment increasing proportions of the original organic matter that had been buried to be oxidized. Under these circumstances most organic carbon is preserved in the un-oxidized portions of beds beyond the main oxidation front. Consequently the proportion of the original organic carbon preserved is dependent upon the reoccurrence frequency of event bed emplacement linked to the rate at which macrofauna are able to colonize the sediment (e.g. Bentley and Nittrouer, 1999). Inevitably the total amount of organic carbon that was preserved in any of these beds is also dependent upon how much organic matter was buried with the sediment in the first place. In the detritus dominated lithofacies encountered here it is likely that at deposition the silt-bearing clay-rich mudstones contained less organic carbon than the clay-rich mudstones. This difference may either be a function of more organic matter being adsorbed on to the higher surface area clay-sized components (see Kennedy et al., 2002) and be a dilution effect (see Tyson, 1995) or where there was greater primary production during deposition of the clay-rich materials (see below).

7.7.2. Organo-minerallic aggregates and the preservation of organic carbon

The clay-, nannoplankton-, and organic carbon-bearing mudstones encountered in this study typically exhibit a very different microfabric style to either the silt-bearing, clay-rich mudstones or the clay-rich mudstones. Specifically, they typically exhibit an organo-minerallic, pelleted fabric in which the individual laminae are discontinuous (Figures 5A, B). This fabric has recently been interpreted as being the depositional product of marine snow aggregates that had been produced in the water column and then settled rapidly to the sea floor by suspension settling (see Macquaker et al., 2010b). In modern fully marine settings most of the fine-grained material that is delivered to the sea-floor is bundled into aggregate grains, which are produced in the water column by a combination of random grain collisions and the effects of filter feeding organisms (e.g. Kranck and Milligan, 1980; Kranck, 1984; McCave, 2005). Marine snow, in the water column is particularly obvious below regions of enhanced primary production, during phytoplankton blooms and in these conditions is responsible for large volumes of organic carbon being delivered rapidly to the sediment surface (see Alldredge and Silver, 1988; Alldredge and Gotschalk, 1990; Lampitt et al., 1993). In the Whitby Mudstone Formation (particularly the Mulgrave Shale Member), the preservation of discontinuous pelleted microfabrics, within the clay-, nannoplankton, and organic carbon-bearing mudstones, is therefore particularly important.

Firstly, it indicates that during intervals when suspension settling was likely the dominant delivery mechanism the sediment was unlikely to have reached the seafloor as a continuous rain of slowly settling fine-grained detritus (compare with Wignall, 1991, 1994; Sælen et al., 1995; Sælen et al., 2000), but rather it was likely delivered as large marine snow aggregates that rapidly settled to the sea bed. Secondly, given the large volumes of aggregates and pellets within the beds that contain these organo-minerallic fabrics it is likely that deposition of these marine snow-rich beds was linked to coincident phytoplankton blooms occurring in the photic zone. The combination of these two processes resulted in large volumes of organic carbon being rapidly delivered to the sea-floor and then buried quickly while the clay, nannoplankton and organic carbon-bearing mudstone were being deposited. During deposition of the Mulgrave Shale Member, where the clay-, nannoplankton and organic carbon-bearing mudstones are the dominant facies, it is likely that high primary organic carbon production, coupled with rapid sediment delivery, contributed significantly to the reasons why large volumes of organic carbon were ultimately preserved in the sediment.

The presence of populations of small framboids within the Mulgrave Shale Member (see also Wignall and Newton, 1998; Newton, 2001; Wignall et al., 2005) suggests that during these phytoplankton blooms, as is the case in modern oceans, anoxia may have developed in the water column. In phytoplankton blooms water column anoxia is a common phenomenon as oxygen demand may exceed oxygen supply under these circumstances (e.g. Shanks and Reeder, 1993; Paerl et al., 1998; Sinninghe Damaste et al., 1998; Kenig et al., 2004; Van Dongen et al., 2006; Macquaker et al., 2010b).

Detailed analyses of the microtextures present in the clay- nannoplankton and organic carbon-bearing mudstones reveals that this facies contains one further interesting textural attribute. Specifically discontinuous silt lags are present at the bases of individual beds (Figure 6). The intimate relationship between the silt lags and marine snow aggregates suggests that a causal relationship may exist between lag emplacement and high primary production in the photic zone. Such a link could result from storms being responsible for both sediment reworking and mechanisms to supply otherwise limiting nutrients to fuel primary production in the photic zone. Storms can be responsible for this dual function either: (a) in settings where storm waves cause water column overturn, which results in seafloor erosion and nutrient recycling from the bottom water layers to the photic zone thereby fuelling a phytoplankton bloom (see Cook and McElhinney, 1979; Hay, 1995; Parrish, 1995; Tribovillard et al., 1996) or (b) where storms on continental shelf are coincident with flood events in the rivers draining the surrounding hinterland in circumstances where both sediment and nutrients are supplied to the continental shelf by the storm event (e.g. Bentley and Nittrouer, 1999; Rotondo and Bentley, 2003).

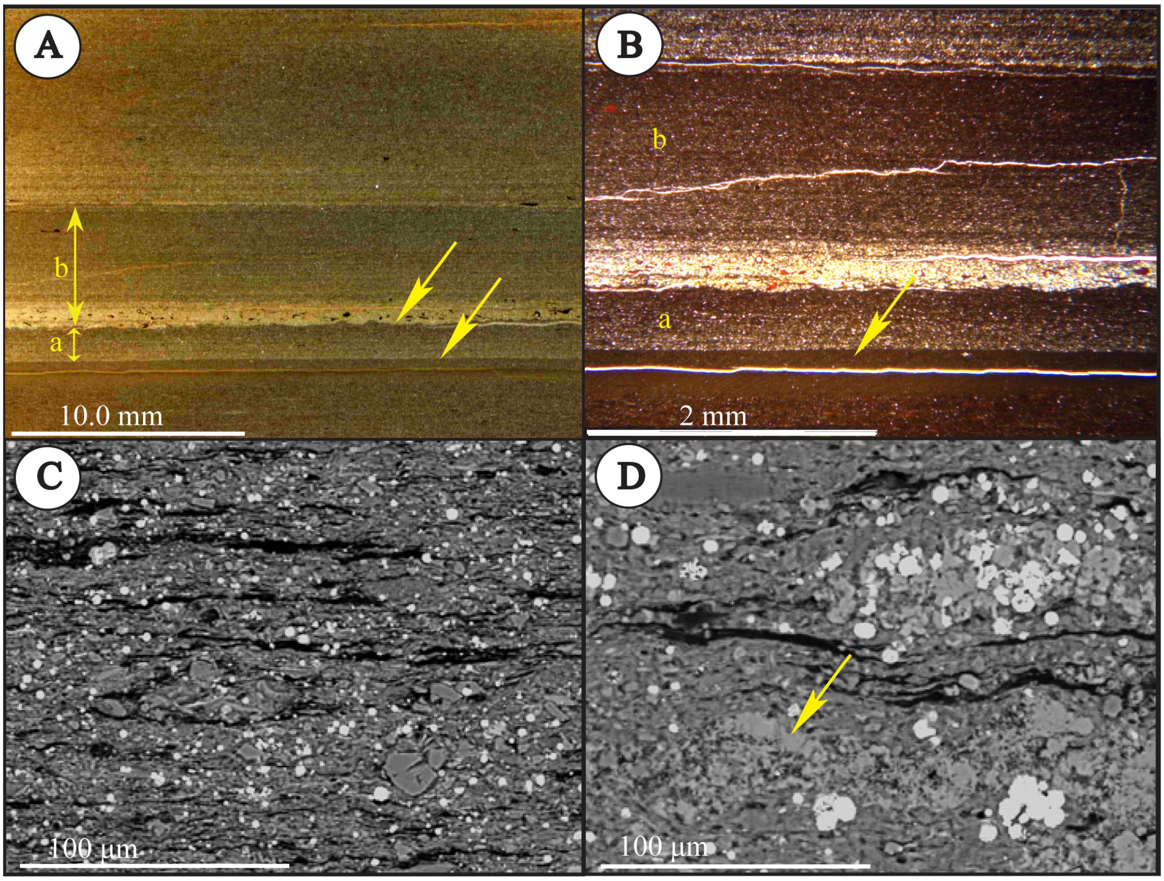

Figure 7.7. A) Thin section scan of a representative thin-bedded and pelleted clay-, calcareous nannoplankton-, and organic carbon-bearing mudstones with homogenised tops (Jet-141). The sample comprises a stacked succession of thin beds (arrowed bases), each with parting spacing less than 10 mm. B) Low-power optical micrograph illustrating the two main depositional beds and their homogenised tops (a and b). Note also the presence of homogenised top of the bed just beneath the bed a (arrow). C) and D) High-power, backscattered electron-optical micrographs of the basal parts of beds in Jet-141 illustrating the abundant organo-minerallic aggregates at the base of both beds a and b respectively. Note the presence of calcite cemented coccolith-rich pellets in D (arrow). Note also that the sample is very rich in organic matter (TOC: 9.34%).

Finally, as our analyses reveal that many of the genetic beds in the Mulgrave Shale Member contain calcareous nannoplankton in addition to detrital fine-grained components, it is reasonable to conclude that during deposition of this interval the balance between clastic dilution and primary production in the water column had changed compared to the conditions that existed during deposition of the underlying Grey Shale Member where clay-rich and silt-bearing clay-rich mudstones predominate. Primary production was likely higher during deposition of the Mulgrave Shale Member and this factor in itself likely also increased the chances of more organic carbon being preserved.

7.7.3. Bioturbation in the Whitby Mudstone Formation – organic carbon preservation and the role of anoxia

It is also quite noticeable that some of the pelleted clay, nannoplankton and organic carbon thin mudstone beds have homogenized tops which are organic carbon depleted relative to their bases. Disruption, of the primary depositional fabrics at these levels indicates that: either the surficial layers of the sediment were being colonized by a meiofauna shortly after deposition but prior to emplacement of the next bed, or that less aggregate material was being delivered to the sea floor towards the end of deposition of each bed. With the latter perhaps coinciding with the sediment contribution from the phytoplankton bloom decreasing causing the relative concentrations of clastic detritus to increase. The presence in the homogenized layer of burrows and the gradational wavy contact between the pelleted organic carbon-rich laminae and the homogenized laminae indicates that the effects of burrow overprinting are likely to be the dominant processes responsible for producing this fabric. In the context of organic matter preservation the presence of homogenized layers at the top of these beds is very important because it indicates that during deposition of the clay-, nannoplankton-, and organic carbon-bearing mudstones: a) there was sufficient time between sediment delivery events for surficial sedimentation colonization (e.g. Macquaker and Howell, 1999) by a diminutive infauna; (b) that much of the organic matter recycling and resynthesis was driven by oxidants diffusing into the sediment pore waters from the water column between deposition events (albeit enhanced by the pore water irrigation effects of burrowing organisms) rather than being available continuously as the sediment was being deposited (this pattern is analogous to that which occurs in burn-downs following turbidite emplacement (e.g. Colley et al., 1984)) and (c) that some oxygen, at least episodically, was present at the sediment water interface during deposition of much of the Mulgrave Shale Member. Together these factors suggest that the large volume of organic matter being preserved in this succession was coupled to episodic delivery of large volumes of organic matter to the seafloor, which in turn was linked to rapid organic carbon burial to depths to which oxidant availability was restricted. Homogenization of the bed tops also suggest that between phytoplankton blooms the water column was at least dysoxic and that the existence of persistent bottom water anoxia, during the deposition of the Anoxic Event preserved within the Mulgrave Shale Member, has been overestimated. This interpretation expands upon the observations of researchers such as Fursich and Oschmann, (1986); Rohl et al., (2001); Rohl and Schmid-Rohl (2005) who reported shell-pavements in this unit, which they too interpreted to be short-lived benthic colonization events.

It is also worth noting that significant amounts of organic matter are also preserved in the Grey Shale Member (up to 3.63% in the silt-bearing clay-rich mudstones and 6.03% in the clay-rich mudstones) much of which is also pervasively bioturbated (see Wignall et al., 2005 and fabrics illustrated in Ghadeer and Macquaker, 2011). The main inference that can be drawn from the observations from the mudstones preserved in this succession is that once produced the organic carbon was best preserved where both degradation and sediment infaunal sediment colonization rates were lower than the reoccurrence frequency of sediment delivery events whether or not these be the distal products of storms or phytoplankton blooms (e.g. Goldring et al., 1991; Bentley et al., 1996; Bromley, 1996; Bentley and Nittrouer, 1999; Macquaker and Howell, 1999; Macquaker et al., 2007; Macquaker et al., 2010b). In addition, enough organic matter had to have been delivered to the sea floor, during the initial phytoplankton bloom, such that the initial thickness of the organic-rich unit was greater than the depth to which subsequently biological mixing and diffusion of oxidants (mainly oxygen and sulfate) could cause homogenization and organic carbon mineralization (e.g. Nittrouer and Sternberg, 1981; Bentley and Nittrouer, 1999). The presence of "frequent marine snow storms" in this succession is therefore likely to have been very important as they ensure that large volumes of organic carbon are delivered to the sediment and that it is buried rapidly by deposition of the next bed.

The Goldilocks condition (see Bohacs et al., 2005), which defines where organic matter was being most efficiently preserved during deposition of the Mulgrave Shale, was therefore operating on temporal scale delineated by the reoccurrence frequency of successive storms and how much primary organic carbon was being produced in the water column. Anoxia in the water column seems to have been a byproduct of this process not the fundamental cause of this process. The situation, however, was rather different during deposition of the Grey Shales when there was both sufficient time between depositional events for organisms to disrupt the primary fabrics and sufficient oxygen in the bottom water layers to fuel the metabolism of organisms present (e.g. Hudson and Martin, 1991; Wetzel and Uchmann, 1998; Macquaker and Howell, 1999; Macquaker et al., 2007). During deposition of the Grey Shales conditions were not in the optimal Goldilocks zone in spite of up to 6.03% TOC being preserved.

Optimising burial and production rates seems likely to have been the main controlling factors of enhanced organic carbon preservation here (see also Kenig et al., 2004; Macquaker et al., 2007).

Finally, the stratigraphic context of the Jet Rock relative to the Grey Shales, suggests that storms operating in the shallow regions of the shelf were dispersing sediment from surrounding shallower regions area down to basinal settings (e.g. Aigner, 1980, 1985; Aigner and Reineck, 1982) and that in physical sedimentological terms the Mulgrave Shale and Grey Shale Members of the Whitby Mudstone Formation exist in an offshore - onshore continuum.

7.8. Conclusions

In order to investigate the main mechanisms responsible for sediment dispersal, delivery and subsequent reworking, which might influence organic carbon preservation in source rocks, the mudstones of the Grey Shales and Mulgrave Shale Members of the Whitby Mudstone Formation exposed in the Cleveland Basin were investigated using optical, electron optical and geochemical methods. Three pertinent, lithofacies types were found including: (a) silt-bearing, clay-rich mudstones (average 1.2%, range from 3.63% to 0.5 %TOC) which were the dominant facies present in the Grey Shales; (b) clay-rich mudstones (average 2.76%, range from 8.69% to 0.67 %TOC) present at the top of the Grey Shales and base of the Mulgrave Members; and (c) clay-, calcareous nannoplankton-, and organic matter-bearing mudstones (average 6.23%, range from 14.2% to 3.25%TOC) which were dominant in the Mulgrave Shale Member. Individual samples were commonly organised into stacked successions of thin (<10 mm), normally-graded, sharp based-beds of each lithofacies types. Within these beds remarkable microtextural variability was found, including evidence of wave-enhanced sediment gravity flows of fluid mud, marine snow aggregates, starved ripple lamination and evidence that the primary depositional fabrics of the sediment were disrupted by diminutive burrowing organisms partially reworking the sediment.

These data indicate that these rocks were deposited in a basin that was gradually deepening but mostly in water depths shallow enough that the sediment could be reworked by waves. Reworking in this context, particularly in the Grey Shales likely generated a lutocline at the base of the water column and this coupled wave activity and prevailing low local gradients resulted in the sediment being dispersed down local slopes by wave-enhanced sediment gravity flows of fluid mud. Surprisingly, analogous; albeit developed in finer grained sediment and within thinner beds are also preserved in the Mulgrave Shale Member. These fabrics coupled with the presence of very thin silt lags indicate that there was much more energy at the sediment water interface than most authors have assumed for this low energy, “basinal” succession.

The data presented here suggest that organic matter preservation here was being controlled by a subtle combination of: (1) sufficient nutrients being available to fuel enhanced primary production in the photic zone, (2) rapid delivery of significant volumes of organic matter to the sediment : water interface as a result of a “marine snow shunt” operating during phytoplankton blooms, (3) deposition of relatively thick events beds that were either formed after storms or phytoplankton blooms (4) rapid burial by deposition of the next bed to minimize the effects of organic carbon mineralization by the top-down colonization of the sediment by an infauna. The evidence that so much of this succession has been bioturbated suggests that the mechanisms that control organic matter preservation in more distal, basinal environments are typically more complicated than most sedimentologists have argued. The prevailing simple model that asserts persistent low energy / anoxia for the preservations for the preservation of organic carbon in this unit is not sustainable.

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Chapter 8

Sequence stratigraphy in organic-carbon rich mudstone successions: a case study of the Whitby Mudstone Formation, NE England

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8.1. Abstract

The Lower Jurassic-aged Whitby Mudstone Formation, in North East England, has been investigated using sequence stratigraphic principles, to interpret how primary production, clastic sediment supply and sediment dispersal interact to control lithofacies variability in this organic carbon-rich succession, which was prone to developing bottom water anoxia.

Using a combination of microscopic (optical and electron optical microscopy of polished thin sections) and whole rock geochemical techniques four mudstone lithofacies were identified. These are: (a) silt-bearing, clay-rich mudstones; (b) clay-rich mudstones; (c) pelleted, clay-, calcareous nannoplankton-, and organic carbon-bearing mudstones; and (d) carbonate cement-rich mudstones. Texturally these mudstones are organised into stacked successions of normally-graded thin beds (<10 mm thick). Internally these beds either exhibit primary depositional microtextures (e.g. ripples, parallel continuous laminae, and discontinuous organo-minerallic aggregate-rich pelleted laminae) or are homogenized. Individual beds are composed variously of clay-sized materials including clay minerals and coccoliths, silt-sized quartz and feldspar, shell fragments, organic matter (up to 14.2%), in addition to pyrite, and carbonate cements. Comparison of successive vertical samples reveals that the beds stack into 0.1 m to 1 m thick upward-coarsening and upward-fining units capped variously by clay-rich mudstones, shell beds, and / or carbonate cement-rich mudstones. Over some intervals, the small-scale upward-coarsening packages are organised into larger scale 1 m to 3 m thick upward-coarsening packages.

We have been able to interpret this succession, even the organic carbon-rich intervals, using sequence stratigraphic principles. Here the small-scale upward-coarsening units, capped by fine-grained units are interpreted to be parasequences. In contrast, the small-scale upward-fining units, capped by carbonate cemented units are interpreted to be transgressive systems tracts; and the large-scale overall upward-coarsening successions are interpreted to be highstand systems tracts. Bacterially mediated cement precipitation occurred during breaks in sediment accumulation just below the major stratal surfaces.

8.2. Introduction and aims

In hand-specimen fine-grained organic carbon rich sediments commonly appear fissile and rarely exhibit any obvious sedimentary structures (e.g. Potter et al., 1980). On the basis of their appearance at this scale, coupled with detailed analyses of their geochemical and paleontological attributes, the facies variability that is present is usually interpreted in terms of changing primary production, varying clastic dilution and changes in bottom water anoxia (e.g. Savrada et al., 1984; Savrada and Bottjer, 1987, 1991; Pedersen and Calvert, 1990; Bottjer and Droser, 1991; Tyson and Pearson, 1991; Wignall, 1994; Tyson, 2001). With these rock attributes in mind, and because individual units with apparently similar characteristics can be traced laterally over wide areas, many geologists have argued that carbonaceous rocks were mainly deposited by suspension settling processes and that individual units exhibit regional, draping geometries (e.g. Tyson et al., 1979; Blanchard et al., 1983; Pye and Krinsley, 1986; Magoon et al., 1987; Rawson and Wright, 1996; Hesselbo et al., 2000; Sælen et al., 2000; Houseknecht, 2001; Hesselbo et al., 2007). In these settings, any subtle changes in vertical facies variability, are typically interpreted in terms of temporal differences in insolation, linked to Kroll-Milankovitch orbital forcing mechanisms (e.g. Haywick et al., 1992; Houseknecht, 2001; Morgans-Bell et al., 2001; Gale et al., 2002; Houseknecht and Kenneth, 2004; Long, 2007; Lia et al., 2008; Bonis et al., 2010; Lenz et al., 2010; Sikhar et al., 2010).

This overarching view has meant that few geologists have thought it would be instructive to investigate how variations in sediment inputs and dispersal mechanisms might contribute to facies variability in organic carbon-rich fine-grained successions in which bottom water anoxia may have played a major role controlling facies variability. In particular, there have only been a few attempts, (e.g. Bohacs, 1990; Pasley, 1991; Creanney and Passey, 1993; Macquaker et al., 1998) to interpret facies variability using high-resolution sequence stratigraphic principles in these units. With the obvious caveat that many investigators have noted that organic carbon enrichment is commonly linked to major transgressions associated with the presence of condensed sections (e.g. Loutit et al., 1988; Pasley, 1991; Wignall, 1991a, 1994; Curiale et al., 1992; Wignall and Maynard, 1993; Macquaker and Jones, 2002).

While fine-grained sediments in hand specimen contain little obvious textural evidence that anything other than suspension settling was the dominant physical process delivering sediment to the seafloor, higher-resolution observations, have enabled important microtextural and mineralogical variability to be imaged (e.g. Macquaker and Gawthorpe, 1993; Wignall et al., 2005). These fabrics include: erosion surfaces, intraclast-rich units, compacted ripple laminae, and triplet fabrics. These structures indicate that during their deposition, the seafloor was being reworked at least episodically, and the sediment was being dispersed by advective processes (both in density flows and as bed load) that were operating both at and near the sediment water interface (e.g. Macquaker and Gawthorpe, 1993; Schieber, 1999; Macquaker and Bohacs, 2007; Schieber et al., 2007; Macquaker et al., 2010a; Ghadeer and Macquaker, 2011). Taken together these observations are important because they indicate that at least some of the sediment was being delivered advectively to sites where accommodation was available. The existence of these mechanisms means that the large-scale sediment-body geometries in organic carbon-rich mudstone successions will not always exhibit draping geometries (e.g. Hallam and Bradshaw, 1979; Cox and Gallois, 1981; Wignall, 1991a, 1991b), but may instead exhibit lateral variability and large scale clinoform geometries (e.g. Asquith, 1983). Assuming that advective dispersal process are operating then these units should be amenable to study using sequence stratigraphic principles (e.g. Asquith, 1983; Bohacs, 1998; Schieber, 1999). To complicate matters further the presence of bed-scale erosion surfaces, that are usually overlooked in hand specimen, suggests that even after it has been deposited the sediment may commonly be reworked prior to reaching its final site of burial. Therefore direct links between primary production in the surface layers and organic carbon-rich sediments may be rather more complex than is readily apparent from their hand specimen appearance. While some researchers have already recognised that advective sediment transport occurs in siliciclastic mudstone successions, particularly in settings where the siliciclastic component is a significant component of the sediment (e.g. Leithold, 1994; Sethi and Leithold, 1994; Macquaker and Taylor, 1996; Schieber, 1998, 1999; Macquaker and Howell, 1999; Macquaker and Jones, 2002; Dalrymple, 2005; Macquaker et al., 2007; Varban and Plint, 2008), there have been few attempts to perform this type of analyses where the sediment is dominated by production-derived components (particularly organic carbon) and deposited in settings where the bottom waters are interpreted to have been persistently anoxic and low energy. Such studies are important because in these circumstances the expression of beds and parasequences (the latter being the fundamental building blocks of sequences (e.g. Van Wagoner et al., 1990)) are likely to be rather different compared to those regions dominated by deposition of clastic inputs. While in the latter upward-coarsening successions of stacked beds capped by marine flooding surfaces are relatively easy to identify, in the former production-derived components may be dominant where clastic dilution was not occurring and the stacking patterns within parasequences may be rather different.

In the light of these comments our aims here are to determine if it is practicable to use sequence stratigraphic principles to interpret the facies variability in mudstones that contain units that are production-detritus-rich, and which have also been interpreted as having been deposited in anoxic bottom waters. We will also discuss the key relationship between early diagenesis and stratal surfaces in these successions. In order to address these issues, we have investigated and compared the organic-rich and organic-poor intervals preserved in the Lower Jurassic-aged Whitby Mudstone Formation exposed on the Yorkshire Coast of North East England (Figure 8.1). This succession is ideal for this study because it is well exposed on a modern wave cut platform, and is relatively unweathered. Crucially, it also contains units that are rich in clastic detritus (the Grey Shale Member), as well as units that are rich in production-derived components (the Mulgrave Shale Member), which were deposited in association with a period in which the basin was prone to developing anoxia (Toarcian Anoxic Event, e.g. Jenkyns and Clayton, 1997). To meet these aims we have:

a) Generated detailed facies descriptions of the mudstones present in the Grey Shale and Mulgrave Shale Members of the Whitby Mudstone Formation using data obtained from optical and electron optical analyses of unusually thin polished thin sections coupled with whole rock geochemical analyses of the same samples.
b) Described the laminae and bedding characteristics of the individual units and the larger scale packages in both organic carbon-rich and organic carbon-depleted parts of the succession.
c) Discussed how the balance of inputs associated with changing production and clastic inputs may have generated the stacking patterns present and how sequence stratigraphic principles might be used to interpret the facies variability in this succession.

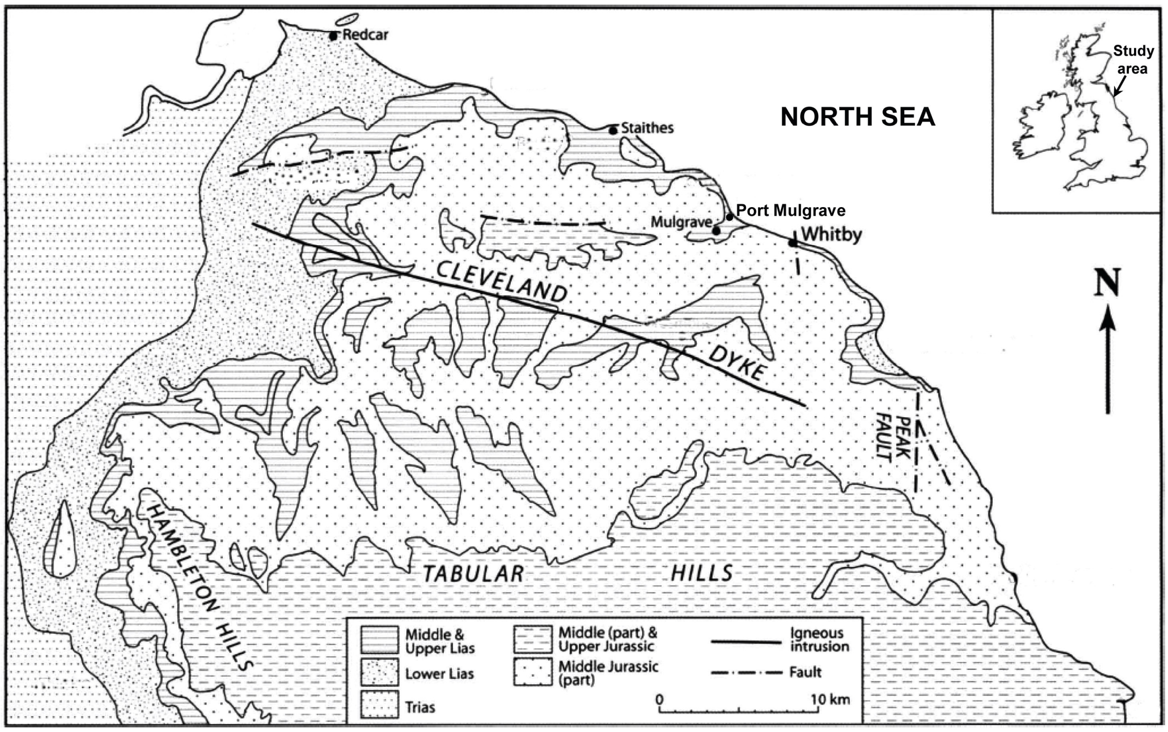

Figure 8.1. Simplified geological map of North East Yorkshire, UK, showing the Yorkshire Coast between Staithes and Port Mulgrave where the Whitby Mudstone Formation is well exposed. (modified from Hemingway 1974).

8.3. The depositional environments of the Whitby Mudstone Formation

The Lower Jurassic of the Cleveland Basin includes the Redcar Mudstone, Cleveland Ironstone and Whitby Mudstone Formations respectively (Howarth, 1962, 1973). The latter, which is the focus of this study, is subdivided into the Grey Shale Member (Beds 1 to 32 inclusive), and the Mulgrave Shale Member (Beds 33 to 40 inclusive). The boundary between the Grey Shale Member and Mulgrave Shale Member was placed at the base of Bed 33 by Howarth (1973). The transition from the Cleveland Ironstone Formation to the overlying Whitby Mudstone Formation is represented by a lithological change from coarse-grained siliciclastic mudstones, and very fine-grained muddy sandstones with sideritic and chamositic shelly ironstones to hard, dark mudstones with calcareous and sideritic nodules (e.g. Howarth, 1973; Rawson and Wright, 1996; Ghadeer and Macquaker, 2011). The Grey Shale Member span the *Dactylioceras tenuicostatum* Ammonite zone (*D. semicelatum* subzone) and the Mulgrave Shale Member span the *Harpoceras falciferum* Ammonite zone (E. exaratum subzone) (e.g. Howarth, 1973, 1992; Powell, 1984). Published rock description of these units are summarised below.

The Grey Shale Member (13 m thick) mainly consists of non-fissile, hard, and medium grey silty mudstones associated with bands of sideritic and calcareous nodules and shell pavements (e.g. Wignall, 1991a; Rawson and Wright, 1996; Sælen et al., 1996; Sælen et al., 2000; Wignall et al., 2005). Much of this part of the succession is intensively bioturbated, although primary depositional structures, such as hummocky cross stratification, wave enhanced sediment gravity flows of fluid mud, parallel lamination and marine snow fabrics are present in some intervals (Wignall et al., 2005; Ghadeer and Macquaker, 2011). In the Grey Shale Member the total organic carbon contents (TOC) average 2.07% (range from 0.53 to 6.03%) (Ghadeer and Macquaker, in review) and hydrogen indices average 250 (HI= mg Hc/g C_{org}) (e.g. Sælen et al., 1996; Sælen et al., 2000; Wignall et al., 2005).

On the basis that the Grey Shale Member mudstones commonly contain: higher than average mudstone TOC contents, sedimentary structures indicative of both current activity and suspension settling, yet are also disrupted by bioturbation. The majority of geologists who have investigated this unit have concluded that it was deposited in a marine basin in which most sediment was delivered by either advective sediment transport processes operating at the seafloor, or by suspension settling out of buoyant plumes, and the bottom / pore waters in the surficial sediment layers varied from dysoxic to oxic. The presence of hummocky cross stratification, shell pavements and wave enhanced sediment gravity flow of fluid mud, however, suggests that storms, at least occasionally, were able to rework and disperse the sediment.

The Mulgrave Shale Member (8 m thick) is commonly described as being composed of a succession of dark to medium grey laminated organic-rich mudstones “black shales” with large bands of calcareous nodules (e.g. Pye and Krinsley, 1986; Rawson and Wright, 1996, 2000; Wignall et al., 2005; Powell, 2010). It includes, an unusual negative excursion in $\delta^{13}C_{(org)}$ in samples that span the lower part of the Member. This excursion is the Toarcian Anoxic Event (e.g. Jenkyns and Clayton, 1997; Hesselbo et al., 2000). This event is also commonly interpreted to be broadly coincident with the extinction of many benthic species (e.g. Kemp et al., 2005; Wignall et al., 2005; Kemp et al., 2006; Cohen et al., 2007; McArthur et al., 2008; Littler et al., 2009; Sabation et al., 2009).

The Mulgrave Shale Member contains significant proportions of organic carbon (TOC) average 5.77% (range from 0.81 to 14.20%, Ghadeer and Macquaker, in review) including woody material (locally called Jet) (e.g. Powell, 1984; Dean, 2007). The hydrogen indices of this organic matter range from 500 to 750 (Sælen et al., 2000; Wignall et al., 2005). Recent high-resolution petrographic observations have demonstrated that these units are much more heterogeneous than is obvious in hand specimen (see Ghadeer and Macquaker, 2011). In particularly this investigation has shown that much of this part of the succession is organised into stacked successions of very thin beds (<5 mm) that exhibit scoured bases and homogenized tops. Internally these beds have complex geometries and variously exhibit parallel lamination, discontinuous wavy lamination, triplet motifs, silt lags and organo-minerallic aggregate fabrics (see also Macquaker et al., 2010b; Ghadeer and Macquaker, in review).

The high hydrogen indices, small framboids, combined with elevated organic carbon contents and extinction of the most species have led most investigators to conclude that the Mulgrave Shale Member was likely deposited in a anoxic / euxinic basinal environment by suspension settling out of buoyant plumes (e.g. Sælen et al., 1995; Rawson and Wright, 1996; Sælen et al., 1996; Jenkyns and Clayton, 1997; Sælen et al., 2000; Kemp et al., 2005; Wignall et al., 2005; Powell, 2010). The recently observed very thin silt lags, homogenized tops, triplet beds, and compacted ripples, however, suggests that physical processes were at least episodically able to dispersing sediment over the seabed (Ghadeer and Macquaker, 2011), and the presence of organo-minerallic textures likely indicates that high primary organic production was occurring in the overlying water column.

The origin of the carbonate cements in these units has been investigated by many researchers (e.g. Raiswell, 1976, 1982, 1987; Coleman and Raiswell, 1981, 1995; Raiswell and Fisher, 2000). Isotopic data for the concretionary carbonate reported in Table 1 by Coleman and Raiswell (1981), for instance, illustrates that the $\delta^{13}C_{carbon}$ values of the calcite cement range from –12.9 to – 15.4%, the $\delta^{13}C_{organic}$ range from – 26.1 to – 37.0% (see also Kemp et al., 2005; McArthur et al., 2008, for isotopic data), while the sulphur isotope ($\delta^{34}S$) values of the framboidal pyrite range from –22 to – 26% and the euhedral pyrite range from –2.5 to – 5.5%. Using these data they concluded that the concretions were likely precipitated from pore waters that had carbon derived from both organic matter and the dissolution of pre-existing shell debris, framboidal pyrite was precipitated in open system sulphate reduction where there is free access of sulphate, and euhedral pyrite was precipitated in pore waters that had only restricted interactions with the overlying sea water sulphur reservoir.

8.4. Materials and methods

The Whitby Mudstone Formation is well exposed between Staithes and Port Mulgrave on the Yorkshire Coast of England (Figure 8.1). The succession at this location was logged and sampled using the published logs of Howarth (1973) and Rawson and Wright (1996) as guides (Figures 8.2 and 8.3). Approximately 90, unweathered samples were collected from the wave cut platform. The samples were collected every 0.25 m throughout the studied interval except over intervals where slumping and weathering had obscured the exposure (Figures 8.2 and 8.3)

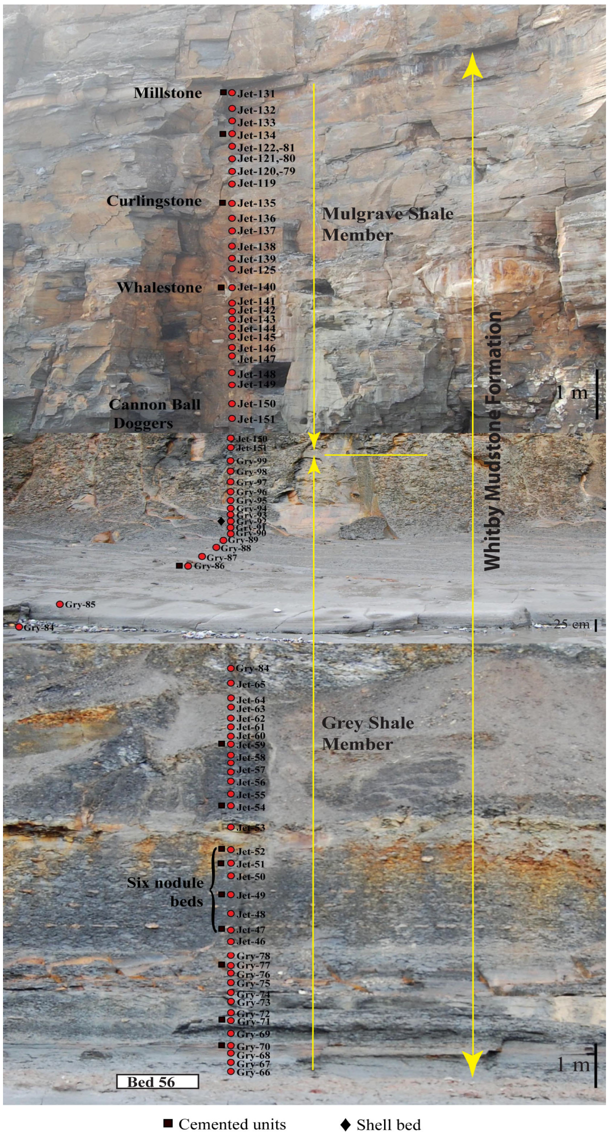

Figure 8.2. Field photographs illustrating the homogenous outcrop expression of the studied Whitby Mudstone Formation, (bottom) and Grey Shale Member. (top) Mulgrave Shale Member (Whitby Mudstone Formation).

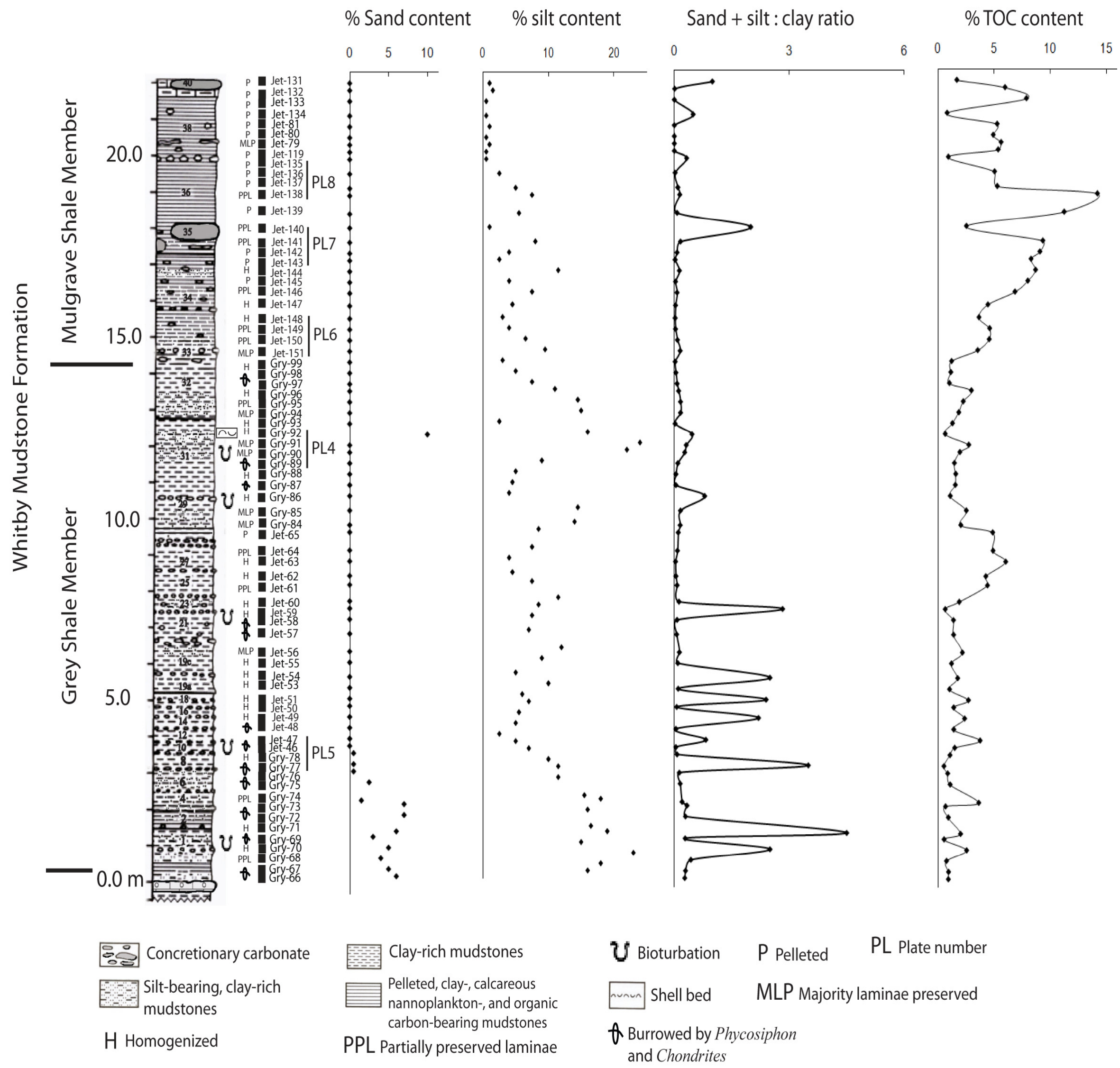

Figure 8.3. Details of the logged and sampled intervals from the Grey Shale and Mulgrave Shale Members (Whitby Mudstone Formation), showing bed numbers (within the log), main microfabrics preserved, collected samples, plate numbers, mudstone lithofacies, sand + silt contents, sand + silt: clay ration, and total organic carbon percentages (TOC). For full rock descriptions, see Table 1. Logs modified from Howarth (1992) and Rawson and Wright (1996). The bed numbers were defined by Howarth (1973).

In order to visualise the bed and lamina scale features, unusually thin (20 µm), large (40 x 60 mm) polished thin sections were prepared from each sample. In order to generate details of 10^{-2} to 10^{-3} m-scale textures present all the samples were firstly scanned into a personal computer using an Epson Perfection 3170 flatbed scanner. Once this had been completed the thin sections were analysed in a conventional petrographic microscope (Nikon Labophot Pol attached to Nikon/D40 digital camera) to determine the variability present within the framework components at 10^{-3} to 10^{-4} m scales. Finally, high-resolution electron-optical analyses were performed using a JEOL 6400 scanning electron microscope (SEM), equipped with backscattered electron detector (BSE) and semi-quantitative, energy-dispersive spectrometer, in order to obtain details of the matrix components at $<10^{-4}$ m scales. The microscope was operated at a working distance of 15 mm, with a beam current of 2.0 nA and a voltage of 20 Kv. The nomenclature scheme outlined by Macquaker and Adams (2003) was used to describe the facies variability present in the sediment.

The bulk-rock mineralogy was performed on all samples utilising a Philips PW 1730 X-ray diffractometer (XRD) operated using copper Ka radiation at 20mA, 40 kV.

The TOC contents of 85 samples were measured using a LECO CS244 carbon analyser. All the samples were powdered and then ca 100 mg was decarbonated utilising 2-3 ml HCL for 8 h at ambient temperature. After that the samples were rinsed 6 times using deionized water and then dried in an oven at 60°C. In order to oxidize the carbon and produce CO_2, all the samples were then heated in a stream of oxygen and the produced CO_2 were measured using an infra-red detector.

Semi-quantitative estimates of the abundances of the different components were obtained by comparing optical and low power backscattered electron images of each sample with published area comparison charts (see Flugel, 2004). To perform this operation initially an estimate of the silt and sand size fraction were made because these are distinctive in the images, then the proportion of pyrite was determined from the backscattered images and finally the proportion of matrix materials were obtained by differences. Semi-quantitative estimates obtained in this way typically have an error of 5% (e.g. Flugel, 2004). This error is much less than the variations in silt and sand contents that in this sample set. Data from these estimates are reported (Table 8.1).

8.5. Results

Using combined petrographic and geochemical techniques four mudstone lithofacies were identified in the Whitby Mudstone Formation. These include (1) silt-bearing, clay-rich mudstones; (2) clay-rich mudstones; (3) pelleted, clay-, calcareous nannoplankton-, and organic carbon-bearing mudstones; and (4) carbonate cement-rich mudstones (concretionary carbonates). In addition, shell beds were observed in two intervals within the upper part of the Grey Shale Member. Thin sections prepared from each sample reveal them to be organised into stacked successions of thin (<10 mm thick) beds. The main microfabrics preserved are summarised in Figure 8.3 (track 2 on the log), and more detailed descriptions of each are given in Table 8.1. The individual mudstone facies variously comprise detrital (allochthonous), production derived (autochthonous) and diagenetic components (e.g. Figures 8.4, 8.5, 8.6, and 8.7). The detrital components are mostly composed of clay-sized materials (mainly illite and mixed layer illite-smectite), with smaller proportions of silt- and very fine sand-sized debris (mainly quartz with minor feldspar). In contrast, the production-derived components are dominated by coccoliths (particularly in the Mulgrave Shale Member), fragmentary shell debris (mainly bivalves with some foraminifer), and organic carbon (up to 14.2% total organic carbon, as amorphous kerogen, woody fragments and algal bodies). Finally, the diagenetic components are mainly composed of pyrite (both framboidal and euhedral) and carbonate cements (siderite, calcite and dolomite). Diagenetic components are present in small volumes in all samples, however, they are dominant at the levels where individual concretions are present (e.g. Figures 8.5A, 8.5B, 8.7A, 8.7B, 8.8A, and 8.8B).

Detailed textural analyses reveal that throughout the succession individual beds are typically sharp-based and normally-graded (e.g. Figures 8.4C, E, 8.7C, and 8.8G). Internally, these beds are either pervasively bioturbated (particularly in the Grey Shale Member, Figure 8.5E, and 8.5G) or have homogenized tops and preserve primary lamination towards their bases (particularly in the Mulgrave Shale Member, see also Ghadeer and Macquaker, 2011). Burrowing here is variously attributed to *Phycosiphon* isp., *Chondrites* isp., *Planolites* isp., and *Palaeophycus* isp. A wide variety of lamina geometries are visible including triplet structures, starved ripples, silt pavements, pellets and organo-minerallic aggregates (Figures 8.4C, 8.4E, 8.7C, 8.7E, 8.8C, and 8.8E).

Detailed comparison of successive units reveals that the lithofacies systematically vary vertically, both on small (0.1 to 1 m) and large (1 to 3 m) scales (e.g. Figures 8.4, and 8.6). For instance, in the Grey Shale Member successive beds stack into overall upward-coarsening units typically composed of homogenised clay-rich mudstones towards their bases, and silt-bearing clay-rich mudstones towards their tops (see depth intervals 9.8 m to 8.8 m and 12.3 m to 11.5 m in Figure 8.3). These small-scale upward coarsening units are in turn stacked into successions that upward-coarsen on a 1 to 3 m scale (Depth interval

12.3 m to 10.9 m, Figure 8.3). These larger scale upward-coarsening successions are capped variously by thin shell beds and silt-bearing carbonate-cement-rich mudstones (depths 10.6 m and 12.3 m, Figures 8.3 and 8.4). Thin overall upward-fining successions are also present (e.g. over depth interval 3.9 m to 3.2 m, Figures 8.3 and 8.5). These typically have silt-bearing clay-rich mudstones at their bases, homogenized clay-rich mudstones towards their top and are also capped by silt-depleted carbonate cement-rich mudstones.

Sample no.	Member	Brief Description	Fine sand	Silt	Clay	Nanno-plankton	Authigenic carbonate	Macro-shell debris	Pyrite	Visible om	Authigenic clay	TOC
			%	%	%	%	%	%	%	%	%	%
Gry-66	Grey Shale	Bioturbated (*Chondrites* isp., *Phycosiphon* isp.) fine sand and silt-bearing, clay-rich mudstone	6.0	16.0	76.5	0.0	0.0	0.0	1.0	0.5	0.0	0.9
Gry-67	Grey Shale	Bioturbated (*Phycosiphon* isp., and *Chondrites* isp.) fine sand and silt-bearing, clay-rich mudstone. The sample preserve some curved laminae.	5.0	18.0	75.5	0.0	0.0	0.5	0.5	0.5	0.0	0.9
Gry-68	Grey Shale	Partially preserve laminae, silt-bearing, clay-rich mudstone with small proportion of sand Beds have erosional lower contacts and upward-fine.	4.0	23.0	68.0	0.0	0.0	2.0	2.5	0.5	0.0	0.7
Gry-70	Grey Shale	Homogenized, fine sand and silt-bearing carbonate cement-rich mudstone	5.0	15.0	8.0	0.0	70.0	1.0	0.5	0.0	0.5	2.5
Gry-69	Grey Shale	Bioturbated (*Planolites* isp. *Phycosiphon* isp.) fine sand and silt-bearing, clay-rich mudstone	3.0	19.0	75.5	0.0	0.0	0.5	1.0	0.5	0.5	0.5
Gry-71	Grey Shale	Homogenized fine sand and silt-bearing, carbonate cement-rich mudstone	6.0	16.5	5.0	0.0	70.0	1.0	0.5	0.5	0.5	2.0
Gry-72	Grey Shale	Bioturbated (*Phycosiphon isp*.) silt-bearing clay-rich mudstone.	7.0	16.0	74.5	0.0	0.0	1.0	1.0	0.5	0.0	0.9
Gry-73	Grey Shale	Bioturbated (*Chondrites* isp., *Phycosiphon isp.*) fine sand and silt-bearing, clay-rich mudstone	7.0	18.0	72.5	0.0	0.5	0.5	1.0	0.5	0.0	0.6
Gry-74	Grey Shale	Partially preserve laminae,thin-bedded, silt-bearing clay-rich mudstone.Thin-beds have erosional lower contacts, have shell bed, and upward-fine.	1.5	15.5	79.0	0.0	0.5	0.0	2.0	1.0	0.5	3.6
Gry-75	Grey Shale	Bioturbated (*Phycosiphon* isp., *Chondrites* isp.) silt-bearing, clay-rich mudstone with some sand	2.5	11.5	84.0	0.0	0.0	1.0	0.5	0.5	0.0	1.0
Gry-76	Grey Shale	Bioturbated (*Phycosiphon* isp.*Chondrites* isp., *Palaeophycus* isp.)silt-bearing, clay-rich mudstone with some preserved gutter casts	0.5	11.5	85.5	0.5	0.0	0.5	0.5	0.5	0.5	0.8
Gry-77	Grey Shale	Bioturbated (*Phycosiphon* isp.and *Chondrites* isp.) silt-bearing carbonate cement-rich mudstone	0.5	10.0	3.0	0.0	83.5	2.0	0.5	0.0	0.5	0.5
Gry-78	Grey Shale	Homogenized clay-rich mudstone with some silt	0.5	7.0	90.5	0.0	0.5	0.0	1.0	0.5	0.0	1.0
Jet-46	Grey Shale	Bioturbated (*Phycosiphon* isp.and *Chondrites* isp.) clay-rich mudstone	0.0	5.0	92.0			0.5				1.4
Jet-47	Grey Shale	Bioturbated (*Phycosiphon* isp.and *Chondrites* isp.) carbonate cement-rich mudstone	0.0	2.5	3.0	0.0	93.0	0.0	0.5	0.0	1.0	3.7
Jet-48	Grey Shale	Partially preserve laminae, bioturbated (*Phycosiphon* isp.) clay-rich mudstone. Beds are upward-fine.	0.0	5.0	93.0	0.0	0.5	0.0	1.0	0.5	0.0	1.4
Jet-49	Grey Shale	Homogenized carbonate cement-rich mudstone	0.0	5.5	2.5	2.0	94.5	0.0	0.5	0.5	0.5	2.3
Jet-50	Grey Shale	Homogenized clay-rich mudstone	0.0	7.0	91.0	0.5	0.0	0.0	1.0	0.5	0.0	1.4
Jet-51	Grey Shale	Homogenized carbonate cement-rich mudstone	0.0	6.0	2.5	0.0	90.0	0.0	0.5	0.5	0.5	2.7
Jet-52	Grey Shale	Homogenized carbonate cement-rich mudstone	0.0	4.0	2.5	0.0	91.5	0.5	0.5	0.0	1.0	3.8
Jet-53	Grey Shale	Homogenized and bioturbated (*Phycosophon* isp.) clay-rich mudstone	0.0	10.0	88.0	0.0	0.5	0.0	0.5	0.5	0.5	1.0
Jet-54	Grey Shale	Homogenized, carbonate cement-rich mudstone	0.0	5.0	2.0	4.0	87.5	0.5	0.5	0.0	0.5	1.7
Jet-55	Grey Shale	Homogenized and bioturbated (*Phycosophon* isp.) clay-rich mudstone	0.0	9.0	87.5	0.0	0.5	0.0	2.0	1.0	0.0	1.2
Jet-56	Grey Shale	Migority laminae preserved, clay-rich mudstone with small proportion of silt.Thin-beds have erosional lower contacts, upward-fine,and contain some ripples near their tops.	0.0	12.0	85.5	0.0	0.5	0.0	1.0	0.5	0.5	2.1
Jet-57	Grey Shale	Bioturbated (*Phycosiphon* isp.and *Chondrites* isp.) clay-rich mudstone	0.0	7.0	90.0	0.0	0.5	0.5	1.0	0.5	0.5	1.3
Jet-58	Grey Shale	Bioturbated (*Phycosiphon* isp.) clay-rich mudstone	0.0	7.5	91.0	0.0	0.5	0.0	0.5	0.5	0.0	1.3
Jet-59	Grey Shale	Homogenized carbonate cement-rich mudstone	0.0	8.5	3.0	4.0	83.0	0.0	0.5	0.5	0.5	0.6
Jet-60	Grey Shale	Homogenized silt-bearing, clay-rich mudstone	0.0	11.5	85.5	0.0	1.0	0.5	1.0	0.5	0.0	1.8
Jet-61	Grey Shale	Partially preserve laminae, clay-rich mudstone. Thin-beds have erosional lower contacts, silt-lags, upward-fine,and some contain triplet motif structures.	0.0	7.5	87.5	0.0	0.5	1.0	2.0	1.0	0.5	4.4
Jet-62	Grey Shale	Homogenized clay-rich mudstone	0.0	4.5	85.5	0.0	0.5	6.0	2.0	1.0	0.5	4.2
Jet-63	Grey Shale	Homogenized clay-rich mudstone	0.0	4.0	91.5	0.0	0.5	0.0	2.0	2.0	0.0	6.0
Jet-64	Grey Shale	Partially preserve laminae,clay-rich mudstone	0.0	7.5	82.0	6.0	2.0	0.0	1.0	1.0	0.5	4.9
Jet-65	Grey Shale	Thin-bedded, pelleted, clay-, calcareous nannoplankton-, organic carbon-bearing mudstones	0.0	8.5	77.0	11.0	1.0	0.0	2.0	5.0	0.0	4.8
Gry-84	Grey Shale	Majority laminae preserved, silt-bearing clay-rich mudstone. Thin-beds have erosional lower contacts, ripples, upward-fine,and some contain triplet motif structures.	0.0	14.0	82.5	0.0	0.5	0.0	2.0	1.0	0.0	2.0
Gry-85	Grey Shale	Majority laminae preserved, silt-bearing clay-rich mudstone. Thin-beds are upward fine and have some ripples.	0.0	14.5	82.0	0.0	0.5	0.0	2.0	0.5	0.5	2.5
Gry-86	Grey Shale	Homogenized, carbonate cement-rich mudstone	0.0	4.0	5.0	0.0	91.0	4.0	0.5	0.0	0.0	1.0
Gry-87	Grey Shale	Bioturbated (*Phycosiphon* isp.and *Chondrites* isp.) clay-rich mudstone	0.0	4.5	90.0	0.0	2.0	2.5	0.5	0.5	0.0	1.5
Gry-88	Grey Shale	Homogenized, clay-rich mudstone	0.0	5.0	91.5	0.5	1.0	0.5	0.5	0.5	0.5	1.5
Gry-89	Grey Shale	Bioturbated (*Phycosiphon* isp.and *Chondrites* isp.) clay-rich mudstone	0.0	9.0	87.0	0.5	1.0	0.5	1.0	0.5	0.5	1.4
Gry-90	Grey Shale	Majority laminae preserved,silt-bearing, clay-rich mudstone. Some beds have erosional lower contacts, silt-lags,and upward-fine.	0.0	22.0	76.0	0.0	0.5	0.0	1.0	0.5	0.0	1.9
Gry-91	Grey Shale	Majority laminae preserved, silt-bearing, clay-rich mudstone. Beds are upward-fine.	0.0	24.0	74.0	0.0	0.5	0.0	1.0	0.5	0.0	2.7
Gry-92	Grey Shale	Homogenized, shell fragment-bearing muddy sandstone (shell bed)	10.0	16.0	54.5	0.0	1.0	18.0	0.5	0.0	0.0	0.6
Gry-93	Grey Shale	Homogenized clay-rich mudstone	0.0	2.5	80.5	0.0	15.0	1.0	0.5	0.0	0.5	1.2
Gry-94	Grey Shale	Majority laminae preserved, silt-bearing, clay-rich mudstone. Beds are upward-fine.	0.0	15.0	83.5	0.0	0.0	0.0	1.0	0.5	0.0	1.8
Gry-95	Grey Shale	Partially preserve laminae, clay-rich mudstone. Beds have erosional lower contacts and upward-fine.	0.0	14.5	83.0	0.0	0.5	0.0	1.0	0.5	0.5	2.2
Gry-96	Grey Shale	Homogenized, silt-bearing, clay-rich mudstone.	0.0	11.0	86.5	0.0	0.5	0.0	1.0	0.5	0.5	2.9
Gry-97	Grey Shale	Bioturbated (*Phycosiphon* isp.and *Chondrites* isp.) clay-rich mudstone	0.0	7.5	89.5	0.5	0.5	0.5	0.5	0.5	0.5	1.0

Table 8.1. Semiquantitative descriptions of each sample analysed.

Sample no.	Member	Brief Description	Fine sand	Silt	Clay	Nanno-plankton	Authigenic carbonate	Macro-shell debris	Pyrite	Visible om	Authigenic clay	TOC
			%	%	%	%	%	%	%	%	%	%
Gry-98	Grey Shale	Bioturbated (*Phycosiphon* isp.and *Chondrites* isp.) clay-rich mudstone with small silt proportion	0.0	5.0	91.5	1.0	0.5	0.0	0.5	0.5	1.0	1.1
Gry-100	Grey Shale	Thin-bedded and laminated clay-rich mudstone. Beds have erosional lower contacts	0.0	3.0	94.5	0.0	0.5	0.0	1.0	0.5	0.5	3.8
Gry-99	Grey Shale	Homogenized, clay-rich mudstone	0.0	3.0	93.5	0.5	1.0	0.0	1.0	0.5	0.5	1.2
Jet-151	Mulgrave Shale	Majority laminae preserved, clay-rich mudstone with some silt proportion. Beds have erosional lower contacts and some contain triplet motif structures.	0.0	9.5	83.0	0.0	2.0	1.0	3.0	1.5	0.0	3.54
Jet-150	Mulgrave Shale	Partially laminae preserve, clay-rich mudstone. Beds have erosional lower contacts, and rippled	0.0	6.5	89.0	0.0	2.0	1.0	1.0	0.5	0.0	4.56
Jet-149	Mulgrave Shale	Partially laminae preserve, clay-rich mudstone. Beds have erosional lower contacts, and rippled upward-fine and some contain triplet motif structures.	0.0	4.0	89.0	0.0	0.5	1.0	2.0	3.0	0.5	4.6
Jet-148	Mulgrave Shale	Homogenized clay-rich mudstone with some proportion of production-derived components	0.0	3.0	86.0	6.0	0.0	0.0	1.5	3.0	0.5	3.65
Jet-147	Mulgrave Shale	Homogenized, clay-rich mudstone	0.0	4.5	92.0	0.0	0.5	0.0	1.5	1.0	0.5	4.45
Jet-146	Mulgrave Shale	Partially preserve laminae,thin-bedded clay-rich mudstone with some silt. Beds are upward-fine	0.0	7.5	88.0	0.0	1.0	0.0	2.0	1.0	0.5	6.86
Jet-145	Mulgrave Shale	Thin-bedded and pelleted clay-, calcareous nannoplankton-, organic carbon-bearing mudstone	0.0	4.0	82.5	6.5	2.5	0.0	2.0	2.5	0.0	8
Jet-144	Mulgrave Shale	Homogenized, silt-bearing, clay-rich mudstone	0.0	11.5	80.5	1.0	0.5	0.0	3.0	3.0	0.5	8.69
Jet-143	Mulgrave Shale	Thin-bedded and pelleted clay-, calcareous nannoplankton-, organic carbon-bearing mudstone	0.0	2.5	78.0	10.0	3.0	0.5	2.5	3.0	0.5	8.29
Jet-142	Mulgrave Shale	Thin-bedded and pelleted clay-, calcareous nannoplankton-, organic carbon-bearing mudstone	0.0	4.0	45.5	30.0	2.0	1.5	3.0	4.0	0.5	9.08
Jet-141	Mulgrave Shale	Thin-bedded and pelleted clay-, calcareous nannoplankton-, organic carbon-bearing mudstone beds have triplet motif, erosional contacts, some ripples, and silt lags on their bases.	0.0	8.0	57.0	26.0	3.0	1.5	2.0	2.5	0.0	9.34
Jet-140	Mulgrave Shale	Partially preserve laminae, carbonate cement-rich mudstone	0.0	1.0	0.5	1.0	95.5	0.0	1.0	0.5	0.5	2.53
Jet-125	Mulgrave Shale	Thin-bedded and pelleted clay-, calcareous nannoplankton-, organic carbon-bearing mudstone	0.0	0.5	74.0	20.0	2.0	0.5	2.0	1.0	0.0	3.65
Jet-139	Mulgrave Shale	Thin-bedded and pelleted clay-, calcareous nannoplankton-, organic carbon-bearing mudstone beds have micro scours and silt-lags at their bases.	0.0	5.5	68.5	20.0	1.0	0.5	1.0	3.0	0.5	11.24
Jet-126	Mulgrave Shale	Thin-bedded and pelleted clay-, calcareous nannoplankton-, organic carbon-bearing mudstone	0.0	0.5	84.5	7.5	2.5	0.5	1.5	2.5	0.5	4.24
Jet-138	Mulgrave Shale	Partially preserve laminae, pelleted clay-, calcareous nannoplankton-, organic carbon-bearing mudstone. some beds have triplet motif structures.	0.0	7.5	66.5	14.0	5.0	0.5	2.0	4.0	0.5	14.2
Jet-127	Mulgrave Shale	Thin-bedded and pelleted clay-, calcareous nannoplankton-, organic carbon-bearing mudstone	0.0	0.5	85.0	5.5	3.0	1.5	1.5	2.0	1.0	3.63
Jet-137	Mulgrave Shale	Thin-bedded and pelleted clay-, calcareous nannoplankton-, organic carbon-bearing mudstone	0.0	5.0	68.0	18.0	4.0	0.5	2.5	2.0	0.0	5.28
Jet-136	Mulgrave Shale	Thin-bedded and pelleted clay-, calcareous nannoplankton-, organic carbon-bearing mudstone beds have some silt lags at their bases.	0.0	2.5	82.5	6.5	1.5	0.5	3.0	2.5	1.0	5.04
Jet-135	Mulgrave Shale	Thin-bedded, pelleted, carbonate cement-rich mudstone	0.0	0.5	1.5	5.5	88.0	0.0	3.5	0.5	0.5	0.92
Jet-119	Mulgrave Shale	Thin-bedded and pelleted clay-, calcareous nannoplankton-, organic carbon-bearing mudstone	0.0	0.5	72.5	20.0	2.5	0.5	2.0	2.0	0.0	5.36
Jet-79	Mulgrave Shale	Majority laminae preserved, pelleted clay-, calcareous nannoplankton-, organic carbon-bearing mudstone. some beds have silt lags (just few grains) at their bases.	0.0	1.0	84.0	8.5	1.5	1.0	2.0	1.0	1.0	5.62
Jet-120	Mulgrave Shale	Thin-bedded and pelleted clay-, calcareous nannoplankton-, organic carbon-bearing mudstone	0.0	0.5	65.5	30.0	0.5	0.5	2.5	0.5	0.0	6.48
Jet-80	Mulgrave Shale	Thin-bedded and pelleted clay-, calcareous nannoplankton-, organic carbon-bearing mudstone	0.0	0.5	71.0	22.0	2.0	0.5	3.0	1.0	0.0	4.92
Jet-121	Mulgrave Shale	Thin-bedded and pelleted clay-, calcareous nannoplankton-, organic carbon-bearing mudstone	0.0	1.0	63.0	30.0	1.5	1.0	2.0	1.0	0.5	6.08
Jet-81	Mulgrave Shale	Thin-bedded and pelleted clay-, calcareous nannoplankton-, organic carbon-bearing mudstone	0.0	1.0	69.5	25.0	1.5	1.5	1.0	0.5	0.0	5.27
Jet-122	Mulgrave Shale	Thin-bedded and pelleted clay-, calcareous nannoplankton-, organic carbon-bearing mudstone	0.0	2.0	54.0	36.5	0.5	4.0	1.5	1.0	0.5	7.86
Jet-134	Mulgrave Shale	Pelleted, Carbonate cement-rich mudstone	0.0	0.5	1.0	0.5	94.5	0.0	3.0	0.5	0.0	0.81
Jet-82	Mulgrave Shale	Thin-bedded and pelleted clay-, calcareous nannoplankton-, organic carbon-bearing mudstone	0.0	0.5	65.0	30.0	0.5	1.0	1.0	1.5	0.5	5.76
Jet-133	Mulgrave Shale	Pelleted clay-, calcareous nannoplankton-, organic carbon-bearing mudstone	0.0	0.5	72.5	20.0	2.0	0.5	2.0	2.5	0.0	7.88
Jet-83	Mulgrave Shale	Thin-bedded and pelleted clay-, calcareous nannoplankton-, organic carbon-bearing mudstone	0.0	2.0	81.0	7.0	2.0	5.5	1.0	0.5	1.0	5.07
Jet-132	Mulgrave Shale	Pelleted clay-, calcareous nannoplankton-, organic carbon-bearing mudstone beds have silt lags (just few grains) at their bases.	0.0	1.5	57.0	36.0	1.5	1.5	2.0	0.5	0.0	5.97
Jet-131	Mulgrave Shale	Carbonate cement-rich mudstone	0.0	1.0	1.0	89.5	7.5	0.5	0.5	0.0	0.0	1.68

Table 8.1. Continued.

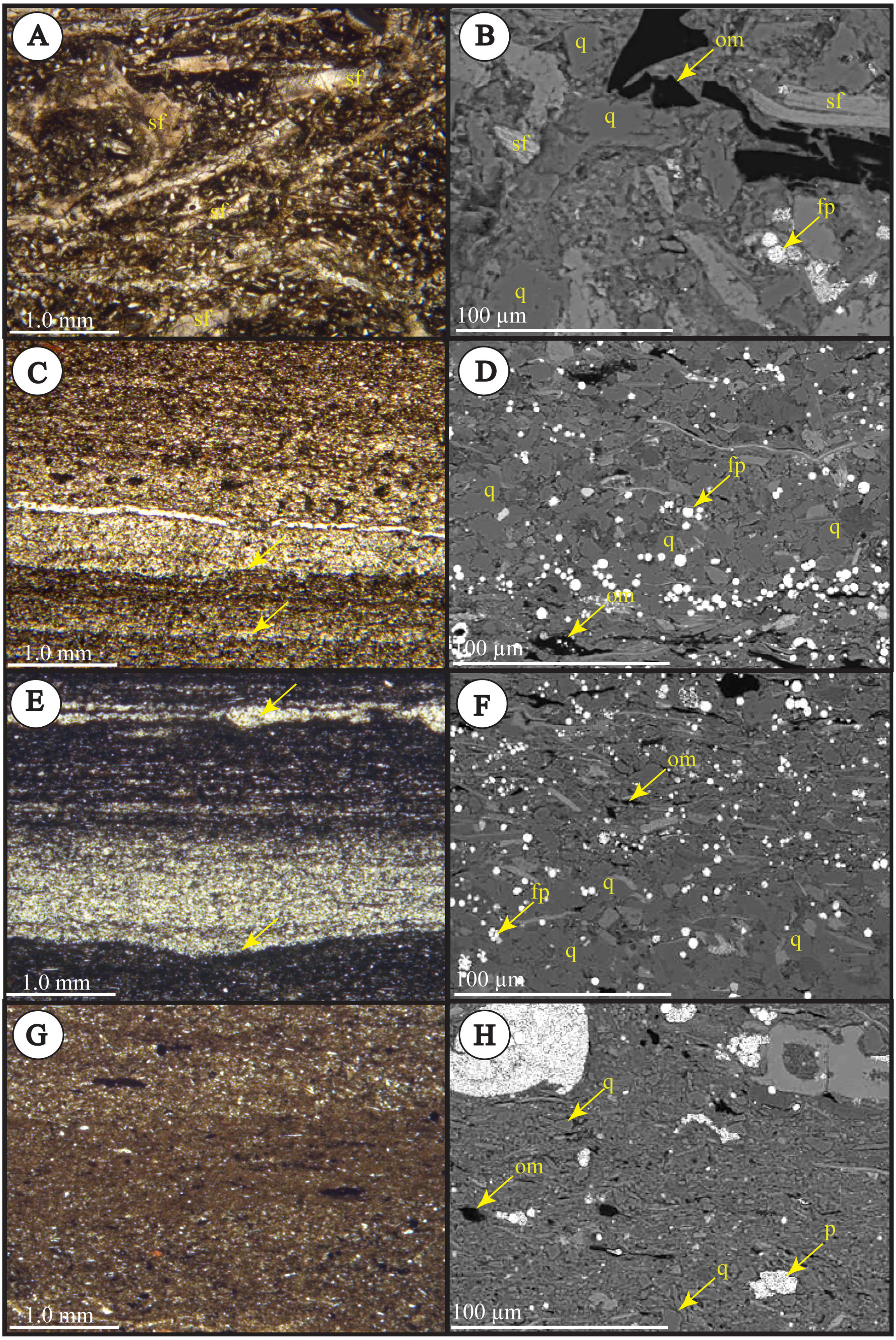

Figure 8.4. (see caption next page)

Figure 8.4. (see previous page): Paired optical and BSE images illustrating the lithofacies variability and stacking patterns through the upper part of the Grey Shale Member (samples Gry-92 to Gry-89, see Figure 3 for sample location). (A and B) Shell fragment-bearing, muddy sandstone (shell bed, Gry-92, TOC: 0.64%). This sample is mainly composed of detrital grains of quartz (q), muscovite, K-feldspar, clay, shell fragment (sf), with minor framboidal pyrite (arrowed fp), and organic matter (arrowed om). (C-D) silt-bearing, clay-rich mudstone (Gry-91, TOC: 2.74%). The sample contains normally graded thin-beds (arrows in C) and is composed predominantly of clay, quartz (q), muscovite, K-feldspar, with some framboidal pyrite (fp) and organic matter (om). (E and F) silt-bearing, clay-rich mudstone (Gry-90, TOC: 1.95%). This sample is organised into normally graded thin-beds with silt lags at their bases (arrows in E) and is mainly composed of clay, quartz (q), muscovite, K-feldspar, with some framboidal pyrite (fp) and minor organic matter (om). (G and H) clay-rich mudstone (Gry-89, TOC: 1.46%). This sample is composed predominantly of clay and amorphous organic matter (om) with minor quartz (q), muscovite, and pyrite.

There is a marked change in facies close to the contact between the Grey Shale Member and the Mulgrave Shale Member. In the former the rock components are mainly composed of fine-grained clastic detritus while in the latter much high proportions of production-derived components are also present (Figures 8.3 and 8.6).

In the Mulgrave Shale Member individual beds are predominantly composed of pelleted, clay-, calcareous nannoplankton-, organic carbon-bearing mudstones. In spite of the dominance of this facies in this part of the succession, large-scale stacking trends are present here too. The expression of these, however, is more subtle and they can only be identified by determining the differing proportions of silt and fine sand in successive samples (Figures 8.3, 8.7 and 8.8). When this is done both meter-scale upward-coarsening and upward-fining packages are evident over depth intervals 18.0 m to 17.1 m and 19.9 m 18.9 m respectively (Figure 8.3). As is the case in the Grey Shale Member, concretionary carbonates in the Mulgrave Shale Member are commonly at the levels where the stacking patterns change (Figures 8.3, 8.7A, 8.7B, 8.8A, and 8.8B).

Figure 8.5. (see next page): Paired optical and BSE images illustrating the lithofacies variability and stacking patterns through the lower part of the succession (samples Jet-47 to Gry-77. see Figure 3 for sample location). (A and B) Jet-47, homogenized cement-rich mudstones; the sample is predominantly composed of siderite (arrowed s) and calcite cement with minor silt-sized quartz, kaolinite (k) and pyrite. TOC: 3.7%. (C and D) Jet-46, bioturbated clay-rich mudstone; the sample is comprises minor silt-sized material (mainly quartz (q), and some k-feldspar) in a matrix predominantly composed of clay-sized materials, amorphous organic matter (om, TOC: 1.49%), and pyrite. (E and F) Gry-78, bioturbated (bio in E) clay-rich mudstone; the sample comprises some silt-sized quartz (q),

muscovite, and K-feldspar in a matrix predominantly composed of clay with minor amorphous organic matter (om, TOC: 1.07%) and pyrite (arrowed p). (G and H) Gry-77, cement-rich mudstone; the sample comprises some fine sand to silt-sized material (mainly quartz (q)) in a matrix mainly composed of calcite, siderite with minor shell fragments (sf) and pyrite (arrowed p) cement. TOC: 0.53%.

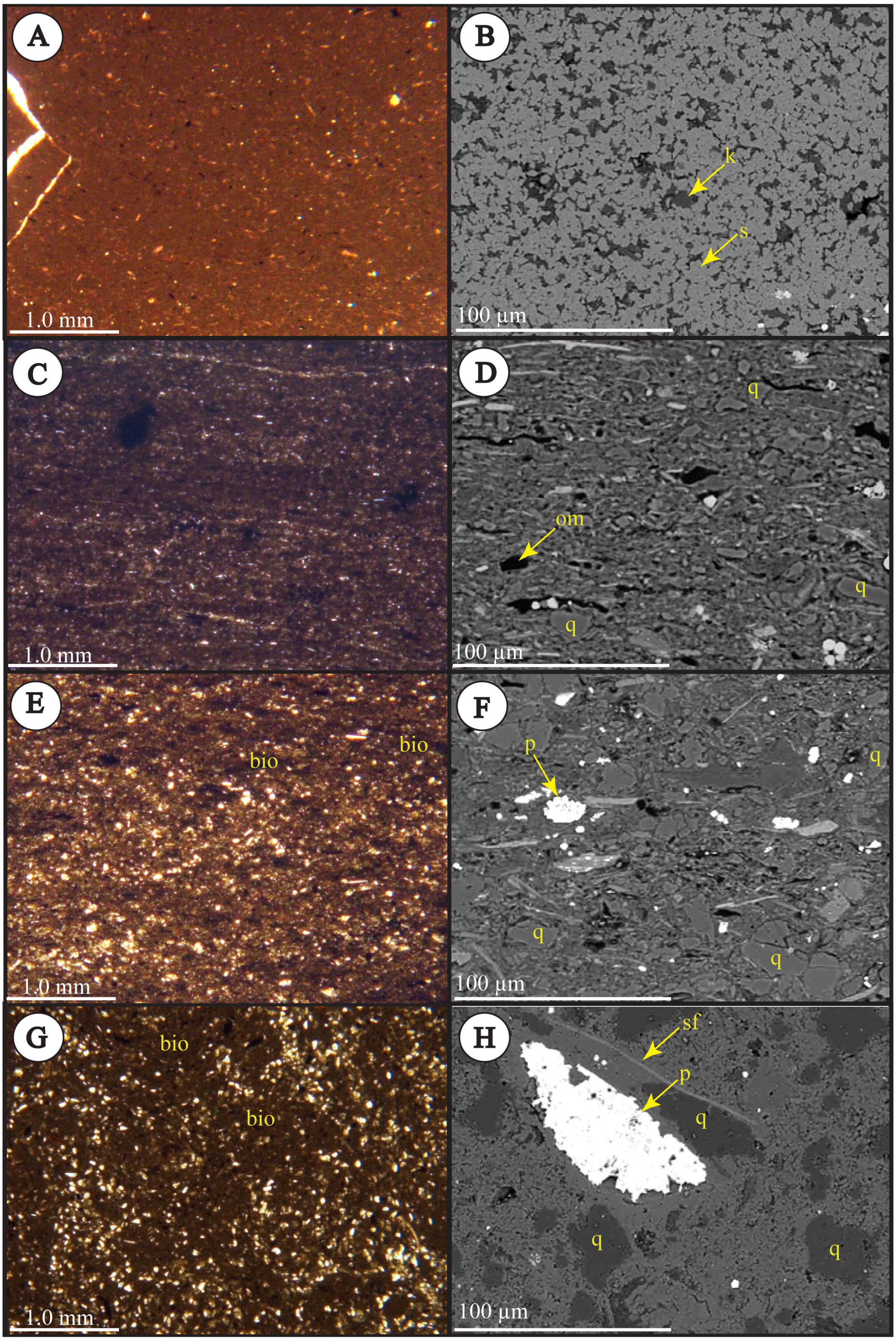

Figure 8.5. (see caption previous page)

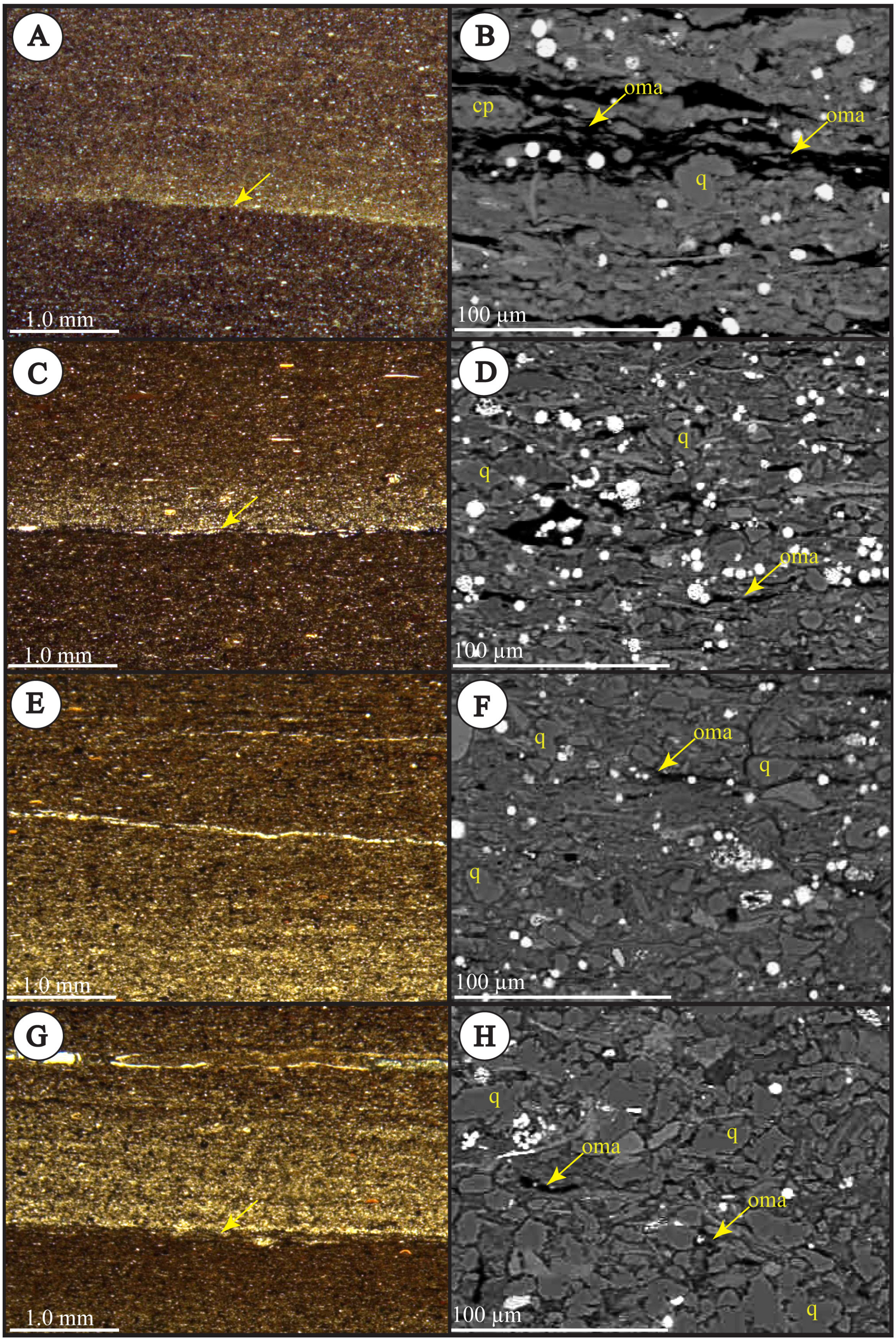

Figure 8.6. (see caption next page)

Figure 8.6. (see previous page): Paired optical and BSE images illustrating the stacking patterns close to the contact between Grey Shale and Mulgrave Shale Members (samples Jet-148 to Jet-151. see Figure 3 for sample location). (A and B) clay-rich mudstone with some production-derived components (Jet-148, TOC: 3.6%). This sample contains a normally graded thin-bed (arrowed in a) and comprises minor silt quartz (q) in a matrix predominantly composed of clay, with some flattened organo-minerallic aggregates (arrowed oma), coccolith-rich faecal pellets (arrowed cp) and pyrite. (C and D) Jet-149, clay-rich mudstone; the sample comprises upward-fining thin-bed (arrow in C) and contains some silt sized material (composed mainly of quartz (q), some feldspar, and minor muscovite) in a matrix of clay-sized material minerals, amorphous organic matter (arrow), small aggregates of calcite, siderite as well as pyrite cements. Note that the sample is very rich in organic matter (TOC: 4.60%) and much of the organic matter is organised into large, flattened wispy aggregates (arrowed oma). (E and F) clay-rich mudstone (Jet-150, TOC: 4.5%). This sample contains silt-sized material (composed of quartz (q), some feldspar and minor muscovite) in a matrix predominantly composed of clay, organic matter aggregates (oma) and pyrite. (G and H) clay-rich mudstone with some silt-sized material (Jet-151, TOC: 3.5%). This framework, silt-sized components in this sample is mainly composed of quartz (q), with some feldspar, and minor muscovite. The matrix component of this sample is mostly composed of clay sized materials, with some calcite, organic matter aggregates (arrowed oma), minor siderite, and pyrite.

Figure 8.7. (see next page): Paired optical and BSE images illustrating the stacking patterns through the middle part of the Mulgrave Shale Member (samples Jet-140 to Jet-143. see Figure 3 for sample location). (A and B) carbonate cement-rich mudstone (Whalestone, Jet-140, TOC: 2.5%). The framework component of this sample comprises minor silt-sized quartz (q) in a matrix predominantly composed of calcite with microsparite texture (arrow), ankerite, some pyrite, and minor organic matter (arrowed om). (C and D) clay-, calcareous nannoplankton-, organic carbon-bearing mudstones (Jet-141, TOC: 9.34%). This sample contains normally graded thin beds (arrows a, b in Figure C) and comprises silt-sized material (composed of quartz (q), and minor K-feldspar) that is preserved in a matrix which is mainly composed of clay, calcite cemented coccolith-rich pellets, organo-minerallic aggregates (oma), and pyrite. (E and F) pelleted, clay-, calcareous nannoplankton-, organic carbon-bearing mudstones (Jet-42, TOC: 9.08%). The sample contains upward-fining thin beds (arrows a, b in Figure E) and comprises some silt-sized material composed of quartz (q), with minor muscovite in a matrix predominantly composed of clay, algal bodies flattened organo-minerallic aggregates (arrowed oma), and organic carbon and coccolith-rich faecal pellets (arrowed cp) as well as pyrite and dolomite cement. (G and H) pelleted, clay-, calcareous nannoplankton-, organic carbon-bearing mudstones (Jet-143, TOC: 8.29%). This sample contains minor silt-sized quartz (q) in a matrix predominantly composed of clay, compacted organo-minerallic aggregates (arrowed oma), coccolith-rich faecal pellets (arrowed cp), and pyrite.

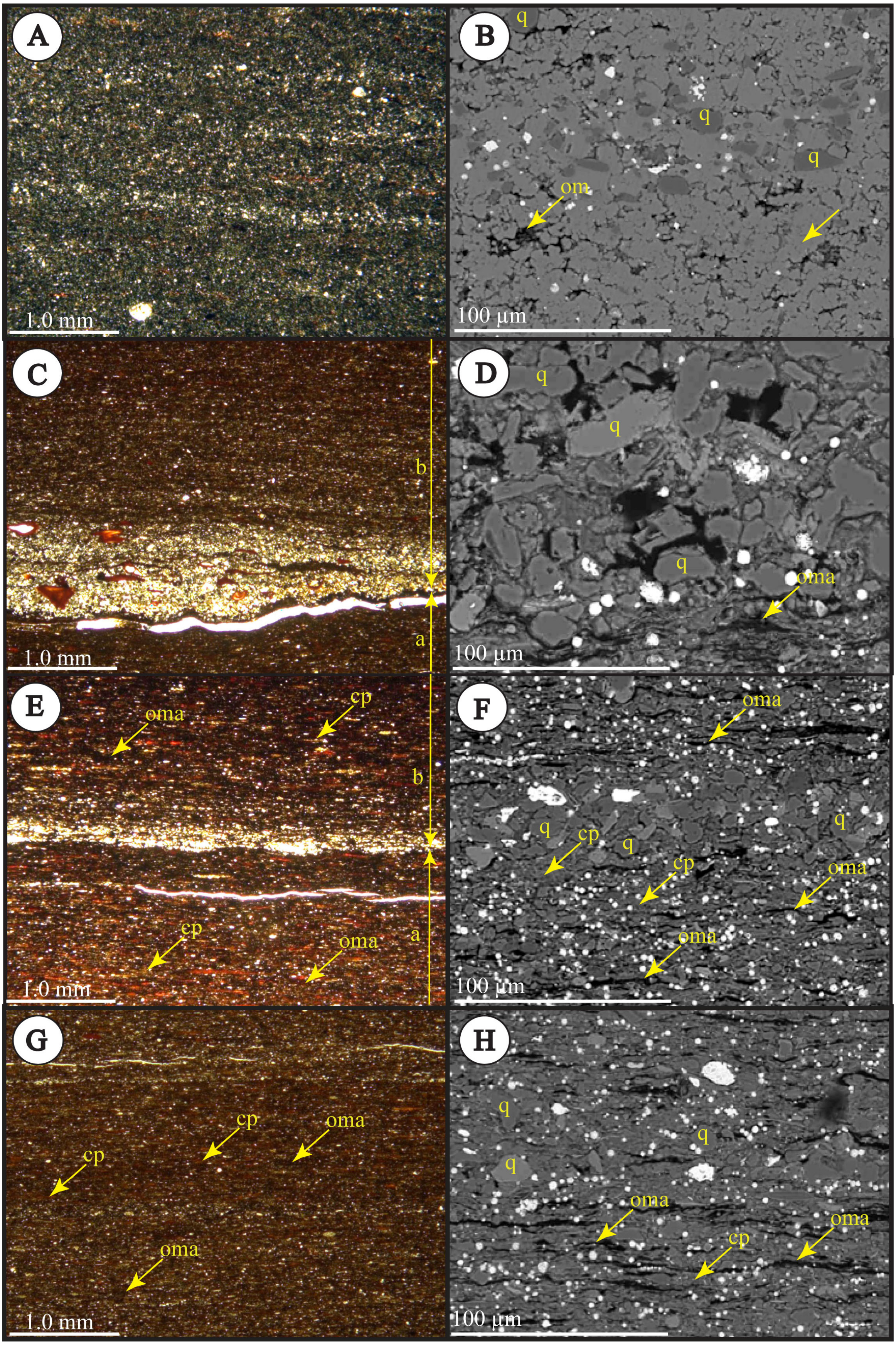

Figure 8.7. (see caption in previous page)

8.6. Discussion

8.6.1. Background to the sequence stratigraphy interpretation

A variety of forcing mechanisms have been proposed as significant factors that might control lithofacies variability and stacking patterns in the rock record. These include sea level change, local tectonics, compaction, weathering, sediment supply, ocean currents, delta switching, and storm frequency (e.g. Van Wagoner et al., 1990; Wignall, 1991; Wignall and Maynard, 1993; Macquaker and Taylor, 1996; Miall, 1997; Van der Zwan, 2002; Macquaker et al., 2007; Nichols, 2009). In any sedimentary basin, sediment will be deposited in locations where accommodation is available and sediment is being supplied. These different processes operate at different scales, with some having only a local effect (e.g. bioturbation, storms) and some having a regional effect (e.g. relative sea-level change, basin structure and growth). Processes such as climate change have an overarching importance because they impact on dispersal processes, sediment supply, and accommodation availability. Numerous authors including (Van der Zwan, 2002; Bonis et al., 2010; Lenz et al., 2010; Sikhar et al., 2010) have proposed that climate has major influence on the facies variability particularly in a transition between different climate states, and then the area will experience regular climate change, from e.g. ice house climate to green house climate, or low to high sediment supply, respectively. Changes in eustatic sea-level tend to lead to changes in accommodation and in turn to the sediment supply to the basin (Miall, 1997), resulting in different facies variability. Sea-level changes relative to land level within a basin may be caused by tectonic subsidence of the basement rather than changes in global sea level creating additional accommodation for sediment to accumulate (e.g. Wignall, 1991; Miall, 1997; Nichols, 2009).

Ocean currents and storm frequency can play very good role in transporting sediments from the site of formation to the site of deposition resulting in different types of sediment variability and stacking patterns. Delta switching, the process by which some rivers change their courses near or on their deltas, can form a type of facies variability by creating a new steeper river channel that forms another delta (e.g. Stanley and Maldonado, 1981; Stanley, 1999; Marshak, 2001).

In the Whitby Mudstone Formation, however, most of these processes are unlikely to result in the stacking patterns that have been observed. Palfy and Smith (2000) have argued that each ammonite zones is of approximate 0.4 – 1.6 Ma duration. Given this time frame the Grey Shale and Mulgrave Shale Members likely span less than 0.5 million years (e.g. Jenkyns, 1985; Cope, 1994; Powell, 2010). Taking into account these observations then the lithofacies variations present in Grey Shale and Mulgrave Shale Members were probably controlled by local forcing mechanisms rather than long term > 5 million years changes in basin configuration. With the later being produced by tectonics or eustatic sea-level change driven by major changes in climate associated with shifts from either ice house to green house conditions. Moreover, the sediments are so heterogeneous that short term climate variations associated with orbital forcing mechanisms are also likely to be on too longer time scales to account for the bed scale heterogeneity.

The presence of microfabrics such as normally graded, ripple laminae, and triplet fabrics, particularly in the silt-bearing, clay-rich mudstones and in the clay-rich mudstones in the Grey Shale Member and basal part of the Mulgrave Shale Member indicates that throughout this interval the sediment was mainly dispersed by storm-induced combined flows. There is little evidence that storm frequencies significantly changed over this part of the successions. The presence of organo-minerallic micro-fabrics and abundant pellets in the Mulgrave Shale Member suggests that water column conditions changed during deposition of the Mulgrave Shale Member. However, given these units are typically still sharp based, normally graded and have silt laminae at their bases it is likely that they too were influenced by storm processes. The changes in the microfabric of these units may reflect a changing balance of primary biogenic production relative to clastic dilution in this part of the succession. Given the decrease in clastic grain size towards the top of the succession this may have been caused simply by the length of the sediment transport path changing over this interval with the Mulgrave Shale Member being deposited in the most distal reaches of the basin compared with the sediments deposited during deposition of the Grey Shale Member.

8.6.2. Stacking patterns and sequence stratigraphy

The majority of the samples analysed here are texturally very heterogeneous at hand-specimen scale. Throughout the Whitby Mudstone Formation this heterogeneity is caused by the hand specimen-sized samples being organised into very thin beds (<5 mm thick), which internally preserve some lamination. The sharp and/or erosive nature of these beds coupled with the presence of compacted ripple laminae and triplet motifs (wave enhanced sediment gravity flows of fluid mud, see Macquaker et al. 2010a) indicates that a significant proportion of the sediment was dispersed, by combined bedload transport at the seafloor, and in fluid mud flows close to the seafloor (see also Ghadeer and Macquaker, 2011, in review). This sediment, in spite of its organic richness was therefore not just being delivered by suspension settling through a low energy water column from buoyant plumes. The ubiquitous presence of these microfabrics produced by advective processes suggests that individual beds are likely to exhibit significant lateral variability produced as they were being transported down sediment transport paths to sites where accommodation was available.

High-resolution analyses of successive vertical samples demonstrate, that individual beds in both the Grey Shale, and Mulgrave Shale Members typically stack into overall upward-coarsening successions that are up to a meter thick (e.g. over depth intervals 12.3 m to 11.5 m, and 18.0 m to 17.1 m, Figure 8.3). These overall upward-coarsening packages are separated from one another by much finer grained units, which in addition to clay minerals in the clay-size fraction may also contain (particularly in the Mulgrave Shale Member) a significant component derived from primary production in the water column (coccoliths and algal-derived organic carbon) (Figures 8.7, and 8.8). In the Grey Shale these upward-coarsening packages (e.g. Figure 8.4) are very similar to those observed in other mud-dominated successions e.g. the Mancos Shale (Macquaker et al., 2007), the Kimmeridge Clay Formation (Macquaker et al., 1999) and the Oxford Clay (Macquaker and Howell, 1999) as well as those present in the Cleveland Ironstone Formation (Macquaker and Taylor, 1996) directly below the studied interval. In the Grey Shale Member, as in all these other examples, these overall upward-coarsening packages are interpreted to be parasequences (*sensu* Van Wagoner et al., 1990). In the Mulgrave Shale Member, while both individual beds and stacked successions of beds can be recognised, the detailed bed-scale stacking patterns are more subtle because so much production-derived material is present. In spite of the complications associated with sediment being derived from other sources and likely from different transport modes (including suspension settling e.g. Macquaker et al., 2010b; Ghadeer and Macquaker, 2011), upward-coarsening stacking patterns, however, can still be identified on the basis of changing proportions of the clastic detritus present (specifically the proportions of detrital very fine sand and silt in the sediment see Figures 8.3).

In the context of performing sequence stratigraphic analyses in organic carbon-rich sedimentary successions, the presence of parasequences both in intervals where clastic inputs supplied the majority of the sediment and where a significant fraction of the sediment was derived from primary production in the water column is very significant. This is because parasequences are the fundamental building blocks of sequences (e.g. Van Wagoner et al., 1990) and their presence in this part of the succession indicates that there is no reason why organic-carbon-rich facies deposited in association with persistent bottom water anoxia and apparently low energy depositional conditions should not be analysed using sequence stratigraphic principles.

High-resolution facies analyses of the Grey Shale and Mulgrave Shale Members indicate that overall upward-fining packages up to meter thick are also present (e.g. over depth intervals 3.9 m to 3.2 m, 15.5 m to 14.5 m, and 19.9 m to 18.6 m, Figure 8.3). These upward-fining units are particularly distinctive because they are capped by carbonate cement-rich units that are depleted in silt. While these upward-fining units are certainly composed of stacked successions of individual beds they are unlikely to be parasequences because the latter typically coarsen-upward (*sensu* Van Wagoner et al., 1990). In the light of this, these upward-fining packages, are interpreted to record systems tract rather than parasequence-scale variability (see Figures 8.5, 8.8) (e.g. Van Wagoner et al., 1990; Macquaker and Taylor, 1996; Macquaker et al., 1999; Macquaker and Jones, 2002; Macquaker et al., 2007). In spite of our samples being collected vertically every 0.25 m, and individual beds being visible the sample spacing in these upward-fining units was at an insufficient resolution to identify the constituent parasequences in this part of the succession.

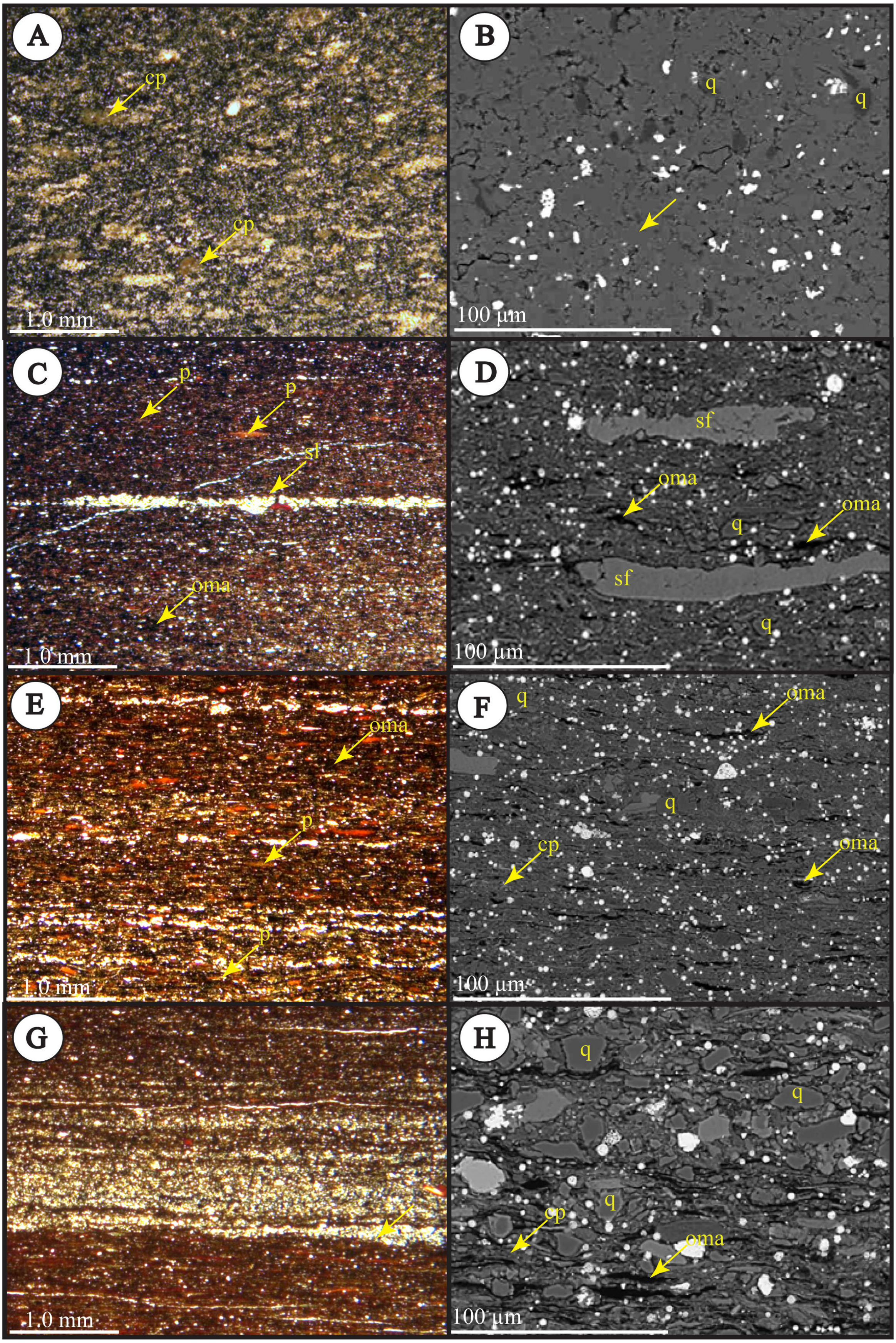

Figure 8.8. (see caption next page)

Figure 8.8. (see previous page): Paired optical and BSE images illustrating the stacking patterns through the upper part of the Mulgrave Member (samples Jet-135 to Jet-138. see Figure 3 for samples location). (A and B) carbonate cement-rich mudstone (Curlingstone, Jet-135, TOC: 0.9%). This sample contains minor silt-sized quartz (q) in a matrix predominantly composed of calcite with microsparite texture (arrow), and pyrite (mostly euhedral). Note the sample contains some coccolith-rich faecal pellets (arrowed cp). (C and D) pelleted, clay-, calcareous nannoplankton-, organic carbon-bearing mudstones (Jet-136, TOC: 5%). This sample comprises silt-sized material (mainly quartz (q)) preserved in a matrix mainly composed of clay, calcite cemented coccolith-rich pellets (p), organo-minerallic aggregates (oma), shell fragment (sf), and pyrite. Note the presence of silt lags (arrowed sl). (E and F) pelleted, clay-, calcareous nannoplankton-, organic carbon-bearing mudstones (Jet-137, TOC: 5.2%). The sample contains some silt sized material (mainly quartz (q) and minor feldspar) in a matrix composed mainly of pellets (arrowed p in Fig. E), algal bodies flattened organo-minerallic aggregates (oma), organic carbon and coccolith-rich faecal pellets (arrowed cp). (G and H) clay-, calcareous nannoplankton-, organic carbon-bearing mudstones (Jet-138, TOC: 14.2%). This sample comprises silt sized material (mostly quartz (q) with minor feldspar) in a matrix predominantly composed of clay, coccoliths rich pellets (arrowed cp), organo-minerallic aggregates (arrowed oma), and pyrite.

Inspection of the log (Figure 8.3) reveals that over some intervals (e.g. over depth intervals 12.3 m to 10.9 m and 17.7 m to 15.5 m) individual parasequences both in the Grey Shale and Mulgrave Shale Members stack into successions that overall upward-coarsen and are capped by cemented units that also contain some silt. These stacked successions of upward-coarsening parasequences are interpreted to be highstand systems tracts (see also Van Wagoner et al., 1990; Macquaker and Taylor, 1996; Macquaker et al., 2007).

Shell beds are also present at the top of the large-scale upward-coarsening successions Typically, shell beds form where there is reduced clastic dilution of the bioclastic components (e.g. Kidwell, 1988, 1989; Xingli and Droser, 1999) and dynamic sediment bypass is occurring. Given this and the fact that the shell horizons in our succession are associated with cement-enriched units, we interpret that these beds to mark the tops of upward-coarsening units that are candidate sequence boundaries.

Figure 8.9 (see next page): Sequence stratigraphic interpretations through the Grey Shale and Mulgrave Shale Members (Whitby Mudstone Formation). Note the presence of coarsening-upward and fining-upward packages throughout the succession. The interpreted stratal surfaces and systems tracts are shown.

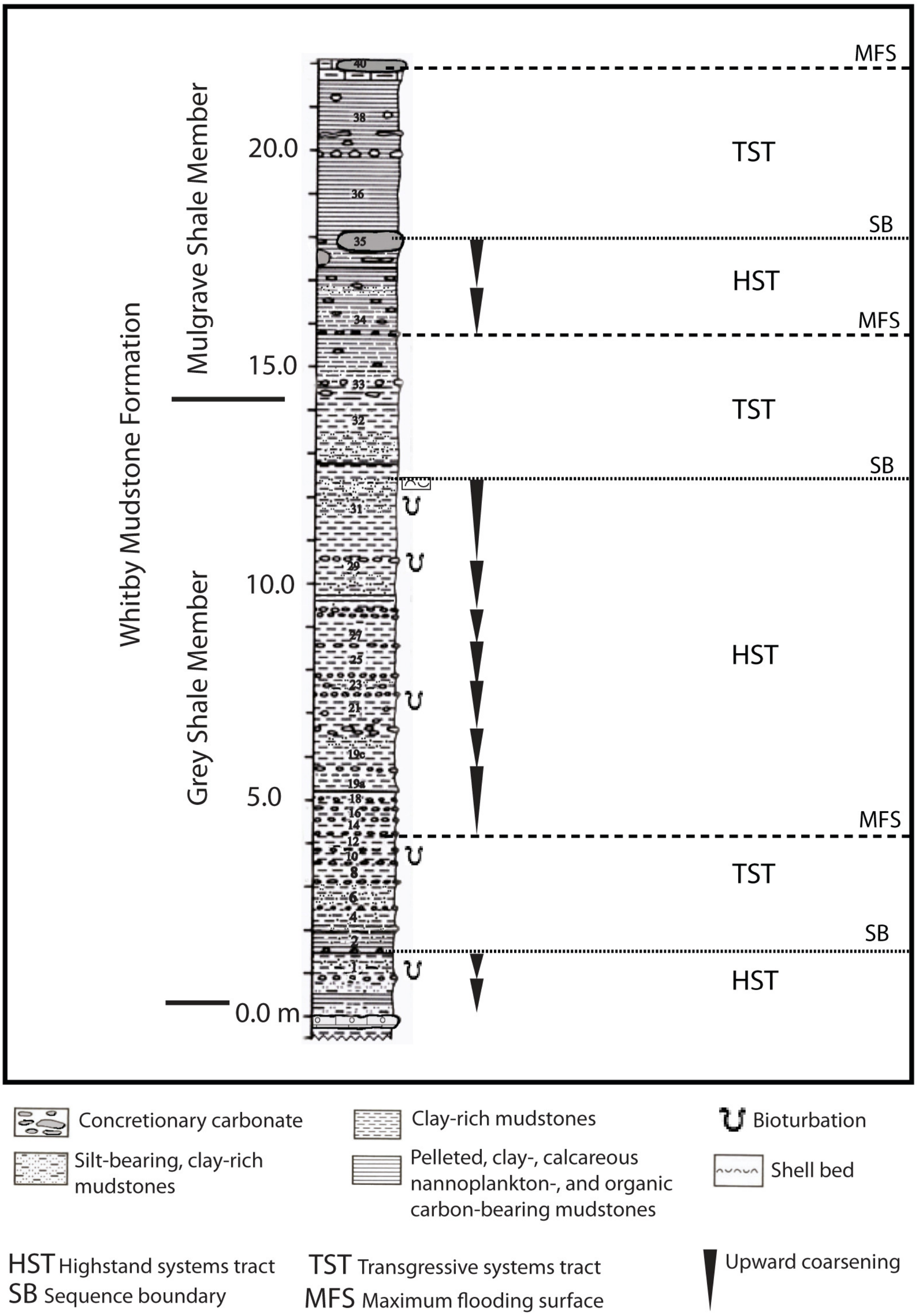

Figure 8.9. (see caption in previous page)

8.6.3. Early diagenesis and stratal surfaces

In this succession the carbonate-cemented units are developed at levels where the large scale stacking patterns change (e.g. Figures 8.7A, B, 8.8A, and 8.8B). The presence of pre-compaction cement assemblages composed of non-ferroan calcite and abundant pyrite, coupled with the published stable isotope data from these units (e.g. Coleman and Raiswell, 1981; Raiswell, 1982, 1987) suggests that cement precipitation at these levels was linked to microbial degradation of organic matter (specifically sulphate reduction) occurring close to the sediment water interface (e.g. Canfield, 1989, 1994; Taylor and Macquaker, 2000a, 2000b; Machent et al., 2007). Early cementation in mud-dominated successions is controlled by the availability of oxidants and reductants (e.g. Canfield, 1989, 1994; Canfield et al., 1993; Macquaker et al., 1996; Taylor and Macquaker, 2000a). Large volumes of cement i.e. to fill the majority of the uncompacted pore space, however, are only present when enough time was available to transport (by diffusion) sufficient solutes to the site of the precipitation to fill the large volumes of pore space (e.g. Curtis, 1987). The occurrence of preferential cemented units just below the stratal surfaces is unsurprising given that these intervals are associated with breaks in sediment accumulation and only at these levels was there enough time to supply the necessary solutes to fill the uncompacted porespace with cement that has a significant component derived from microbial-mediated degradation of organic carbon (e.g. Taylor and Curtis, 1995; Taylor et al., 1995; Macquaker and Taylor, 1996; Macquaker et al., 1996; Taylor and Macquaker, 2000a; Macquaker and Jones, 2002). In this context the cemented units that contain some silt at the top of the coarsening-upward successions are likely associated with sediment bypass (Figure 8.9) (e.g. Macquaker and Jones, 2002; Macquaker et al., 2007) and be broadly coincident with sequence boundaries, whereas those units that cap the overall fining successions that are silt depleted are candidates for maximum flooding surfaces / condensed sections (see Figure 8.9) (see also Macquaker and Taylor, 1996; Macquaker and Howell, 1999; Macquaker and Jones, 2002).

8.7. Conclusions

Lithofacies variability analyses using field observations and optical, electron optical, and geochemical techniques with Lower Jurassic organic-rich, mudstone-dominated successions from the Cleveland Basin have been undertaken. By using these techniques four lithofacies were documented based on the different proportions of components derived from primary production, clastic, and chemical processes that each contains. These are: a) silt-bearing, clay-rich mudstones, b) clay-rich mudstones, c) pelleted, clay-, calcareous nannoplankton-, and organic carbon-bearing mudstones, and d) carbonate cement-rich mudstones.

Microtextural analyses of thin sections reveal that the individual genetic beds are mostly sharp-based and normally-graded (< 10 mm thick) and were probably the distal products of storm reworking and storm induced advective transport. These beds are predominantly composed of detrital clay, silt, very fine sand, and in more production-dominated facies, are mainly composed of coccoliths, organic carbon, and shell debris in addition to pyrite and carbonate cements.

Despite not being obvious from their appearance in the field and in hand specimen, detailed comparison of successive vertical samples from both detrital-dominated and productivity-dominated successions indicates that individual beds stack systematically on both small (decimetre – metre) and large (metre) scale. These stacking patterns can be recognised both in the production-rich intervals and those dominated by detrital components. The small-scale upward-coarsening units are interpreted to be parasequences; the small-scale upward-fining units are interpreted to be transgressive systems tracts; and the large-scale upward-coarsening units are interpreted to be highstand systems tracts.

The presence of early pre-compaction cements at the location where the stacking patterns change from overall upward-coarsening to upward-fining and vice versa is interpreted to indicate that these units were subject to prolonged breaks in sediment accumulation associated where bacterially mediated metabolic processes that supplied a significant proportion of solutes for cement precipitation. The silt-depleted cemented units at the top of upward-fining packages are interpreted to be maximum flooding surfaces; in contrast to those that are enriched in silt and shelly material at the top of upward-coarsening packages which are interpreted to be associated with clastic bypass and sequence boundaries.

This study demonstrates that even organic carbon-rich rocks whose deposition is commonly linked to the presence of bottom water anoxia and sediment delivery from suspension settling processes are still amenable to sequence stratigraphic analyses.

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Section 3:

Synthesis and conclusions

Chapter 9

Synthesis, conclusions, and recommendations for further research

In this chapter, I summarise the key findings of each of the papers presented in Section 2 and the wider implications of this study in the light of aims outlined in Chapter 1. I have also considered some of the research questions that are raised by this study.

9.1. Synthesis and Conclusions

The processes responsible for controlling the fundamental facies variability in ancient mud-dominated basins are relatively poorly known. Historically, most researchers have argued that muddy materials are produced by a combination of detrital inputs to the basin, from the reworking of ancient landscapes by weathering and erosion, primary production in the water column and diagenesis once the grains have been produced. The fine grain size of these materials, coupled with the fact that they apparently exhibit little obvious variability in hand specimen, and individual units with similar lithofacies can be traced laterally over many kilometres, has led many investigating geologists to conclude that after being produced this materials settled from buoyant plumes as a continuous rain of material thorough a low energy water column and the facies exhibit draping geometries at basin-scales. Additionally, where the rocks contain elevated concentrations of total organic carbon (>2 %, i.e. are source rocks) and preserve primary lamination it is commonly argued that the sediments were deposited in regions where the bottom waters were anoxic to minimise the amount of oxic degradation (particularly by macro-organisms using aerobic respiratory processes), and maximise the preservation of organic carbon.

Recent work utilising high-resolution optical, electron optical and geochemical techniques, however, has demonstrated that at least some muddy successions are much more texturally heterogeneous, at sub-hand specimen scales, than previously noted. In particular this research demonstrates that these successions are commonly organised into stacked successions of very thin (<10 millimetre thick) sharp-based, normally-graded beds and that these beds either contain diminutive ripples, erosion surfaces, triplet fabrics and / or have been homogenized by burrowing organisms. These microfabrics indicate that the sediment was being dispersed advectively around the basin by a combination of bed load transport and density currents prior to deposition. Furthermore, analyses of successive samples collected vertically through mud-dominated successions, even those that appear similar in hand specimen has revealed that these stacked successions of thin beds are organised into relatively thin (<1 metre) upward-coarsening packages that are capped by units where the grain sizes abruptly decrease. On the basis that these packages are similar, albeit developed in finer grained facies, to the upward coarsening bedsets present in coarser sedimentary successions, these units have been interpreted to be parasequences. In addition, individual parasequences stack into successions that overall upward-coarsen and upward-fine on approximately a 1 to 5 metre scales and that at the inflexion points between the larger-scale stacked patterns the sediment commonly contains significant diagenetic components. Using the patterns present in coarser siliciclastic sediments as a guide these larger-scale packages have been interpreted to be systems tracts and specifically: where they are composed of overall upward-coarsening parasequences - highstand systems tracts, and where they comprise overall upward-fining parasequences - transgressive systems tracts respectively; with the cemented units being developed at stratal surfaces variously sequence boundaries and maximum flooding surfaces. Finally, the cemented units are interpreted to be developed in association with breaks in sediment accumulation at the stratal surfaces.

These data indicate that mudstones are much more heterogeneous than most authors have argued and that this heterogeneity is systematic and can be interpreted using sequence stratigraphic principles. In spite of these developments many authors continue to argue that facies variability in organic carbon rich mudstones should be interpreted in terms of variations in primary production and clastic dilution coupled with the existence of persistence of long term bottom water anoxia. If this is the case there is an apparent disconnect between organic carbon-rich muddy successions deposited in basin centres that are currently being interpreted in terms of changing primary production and anoxia and clastic-rich muddy successions that are being interpreted in terms of sequence stratigraphic principles typically in muddy shelf environments. Given this paradox, the question inevitably arises: where, in a larger scale basin context, do you stop interpreting updip mudstones in terms of sequence stratigraphic principles and start to interpret them using primary production clastic dilution and anoxia? Moreover is it possible to perform sequence stratigraphic analyses in down-dip successions and link all the sediments being deposited in a basin within a unified facies model?

In order to address this problem three specific aims were identified for this research, each of which are presented as a separate paper, as components parts of this thesis, including: (a) Are the transport process that occur to disperse muds deposited in different parts of an individual basin similar? Specifically, can up-dip dispersal mechanisms in coarse-grained mudstones be recognised down-dip in very fine-grained mudstones? (b) What physical, chemical and biological processes control organic carbon preservation in basins in organic carbon-rich sediments if the sediment was bioturbated? (c) Are successions that contain organic carbon-rich mudstones amenable to study using sequence stratigraphic principles or are they disconnected from sediments up-dip and therefore should indeed be considered as separate entities because their variability is not ultimately controlled by the same processes although these different conditions do develop during periods of relatively high sea-level.

The Lower Jurassic succession from the Cleveland Ironstone Formation to the Whitby Mudstone Formation was chosen to investigate these problems. This interval is an ideal natural laboratory for this study, as it is siliciclastic mudstone dominated and the units are well-exposed on coastal exposures on the Yorkshire Coast of NE England. In addition, previous researchers have argued that these strata were deposited in settings ranging from offshore transition (Cleveland Ironstone Formation), through offshore mudstones (Grey Shale Member) to basinal anoxic (Mulgrave Shale Member) environments.

Utilising combined field observations, thin sections observations (obtained at scales ranging from 10^{-3} to 10^{-6} m using optical and electron optical (backscattered electron imagery) and whole rock geochemical methods (XRD, total organic carbon analyses) on 151 samples collected every 0.25 m; six lithofacies were identified. These include: (1) sand- and clay-bearing, silt-rich mudstones which were rarely identified, being only present below some of the cement-rich mudstones in the Cleveland Ironstone Formation; (2) silt-bearing, clay-rich mudstones which were commonly encountered in the Cleveland Ironstone Formation and are subordinate components of the Grey Shale Member; (3) clay-rich mudstones which are the dominant component of the Grey Shale Member and lower part of the Mulgrave Shale member and a subordinate component of the Cleveland Ironstone Formation; (4) clay-, calcareous nannoplankton-, and organic carbon-bearing mudstones which are the main lithofacies of the Mulgrave Shale Member and were found at only a few levels in the upper part of the Grey Shale Member; (5) fine-grained muddy sandstones which were only rarely encountered in the studied succession being identified only at the base of the Cleveland Ironstone Formation; and (6) cement-rich mudstones are widely encountered throughout the studied succession. Shell beds were also recognised in some intervals within the upper part of the Grey Shale Member.

Texturally, a wide variety of primary sedimentary fabrics are preserved in these mudstones, where they have not been homogenized by bioturbation. The mudstones throughout the successions are typically organized into individual thin genetic beds (single depositional events *sensu* Van Wagoner et al., 1990) that are commonly < 10 millimetres thick. The individual beds are typically normally graded and have sharp / erosional bases with vertical relief up to 5 mm, and internally exhibit a variety of lamina geometries. Internally, the beds are typically organized into either lamina-sets that comprise thin intercalated layers of silt and clay laminae, or form pelleted, discontinuous wavy laminae. The laminae towards the bed bases are straight, curved, or wavy and non-parallel and may down-lap onto the underlying bedding planes. Some of them comprise very fine sand and silt-sized material predominantly composed of quartz and feldspar that are developed into basal silt lags. Gutter casts in which lamina onlap on the scour margins, and ”triplet motifs” (erosional bases, homogenous basal layers that are abruptly overlain by intercalated silt and clay lamina before being draped by clay-sized material that is variously bioturbated) are also present. At some levels beds become more pellet-rich and are either composed of clay-sized minerals or dominated by nannoplankton debris. In these units the microfabrics change significantly as the middle portions of the beds are increasingly organised into organo-minerallic, pelleted, discontinuous wavy lamina rather than just forming thin lamina-sets composed of intercalated clay and very fine silt.

The presence of thin, normally graded, sharp-based beds with homogenized tops throughout the studied succession is very important. Their existence even in very organic carbon-rich units indicate that the sediment delivery to the site of deposition was episodic and that during deposition there was both sufficient time and oxygen available between storm events for sediment reworking and infaunal colonization of the recently deposited sediment prior to the following the sediment delivery episode.

The presence of different internal laminae geometries within these facies indicates that the sediment was delivered by both advective processes and suspension settling out of buoyant plumes. The different microfabric styles indicate that sediment was being reworked and dispersed by the effects of distal storms, by geostrophic flows, and by density flows such as wave-enhanced sediment gravity flows of fluid mud. Moreover, the existence of starved, low angle ripple laminae even in the "anoxic" basinal part of the succession further attests to the presence of traction currents and turbulent reworking of the sediments during deposition and sedimentation. These overall structures indicate that conditions at the sediment water interface were at least occasionally very energetic, and mud dispersal was not just being accomplished by low energy suspension settling out of buoyant plumes where bottom waters were precisely anoxic.

Based on the observations of thin-beds with silt lags at their lower contacts, partial bioturbation, ripple laminae, triplet motif structures, organo-minerallic, pelleted discontinuous laminae and abundance of surface-water-derived components (e.g. coccoliths and organic matter) in the organic-carbon-rich mudstone lithofacies preserved in this succession does suggest that the mechanisms that control organic matter preservation in more distal, basinal environments are much more complicated than most geologists have assumed. Here, where bioturbation has not overprinted the primary fabrics pelleted-rich laminae that contain organo-minerallic aggregates are commonly observed. These aggregates are interpreted to be the ancient depositional product of marine snow / phytodetritus produced in the water column and then settled to the sea floor rapidly. In the studied succession, where these organo-minerallic-aggregates are present, it is likely, as in modern environments, that the majority of the sediments in suspension were delivered episodically to the sediment / water interface either from storm driven mixing of the water column or from flood events in rivers that coincided with the occurrence of storms on the shelf and buried rapidly, prior to being significantly mineralised in the oxic zone by subsequent sediment colonization between delivery episodes. Moreover, the abundance of marine snow fabrics suggests that once produced organic matter was delivered to the sea floor in aggregates rather than as individual grains, by suspension settling processes and that marine snow formation played a major role in the organic carbon enrichment in this succession. Instead of the simple model that asserts persistent low energy and bottom water anoxia for the preservation of organic matter, the existence of this material suggest that enhanced organic production in the water column, coupled with episodic and rapid sedimentation rates were the key factors controlling organic-matter enrichment in this particular ancient organic carbon-rich succession. There is no doubt that water column anoxia may have occurred during this interval, however, it was not persistent and was likely a byproduct of high primary production rather than being a pre-requisite for organic carbon preservation.

Detailed high-resolution analysis of successive units preserved in a more distal, basinal environment reveals that the fine-grained and organic carbon-rich mudstone lithofacies vary systematically throughout the studied succession despite their apparent homogeneity at hand specimen scale. Here, successive samples were found to stack vertically into 0.1 m to 1m scale upward-coarsening and upward-fining units that are capped variously by clay-rich mudstones, shell beds, and carbonate cement-rich mudstones. In some intervals the small scale upward-coarsening packages were also found to stack into large scale upward coarsening packages that are capped by cemented units. While these stacking trends can be easily recognised in the Grey Shale Member being mainly controlled by fine-grained clastic detritus components, their recognition in the Mulgrave Shale Member, where production-derived components are dominant, can only be identified by determining the differing proportions of fine sand and silt within pelleted, clay-, calcareous nannoplankton-, organic carbon-bearing mudstone facies. In the light of these observations, the small-scale coarsening-upward units are interpreted to be parasequences; the small-scale fining-upward packages are interpreted to be transgressive systems tracts; and the large-scale coarsening-upward packages are interpreted to be highstand systems tracts. Pre-compaction carbonate cemented units are present at the levels of candidate stratal surfaces.
With the cemented units that are rich in silt and shelly material and capping the upward-coarsening successions being interpreted to be sequence boundaries probably associated with clastic sediment bypass; while the cemented units that are depleted in silt and capping upward-fining successions are interpreted as probably having been maximum flooding surfaces. The high proportion of non-ferroan calcite and pyrite, coupled with the published stable isotopic data from these cemented units (light $\delta^{13}C_{carbon}$ range from –12.9 to –15.4%, $\delta^{34}S$ of framboidal pyrite range from –22 to – 26% and euhedral pyrite range from –2.5 to – 5.5%, see Coleman and Raiswell, 1981; Raiswell, 1982, 1987) indicates that

bacterially mediated processes occurring close to the sediment water interface were most likely responsible for cement precipitation.

The systematic variations in grain size and the micro-textural attributes of the sediments present throughout this succession suggests that sequence stratigraphic principles can be also applied to interpret the lithofacies variability even in organic carbon-rich mudstone lithofacies whose deposition has previously been linked with the development of persistent bottom water anoxia in low-energy environment.

Overall, this high-resolution study reveals that the mechanisms that underpin sediment dispersal, lithofacies variability and organic matter enrichment within mud-dominated succession preserved in the Lower Jurassic Cleveland Basin are much more complicated, being controlled mainly by the complex interplay between clastic input, production in the water column and at the sediment water interface, bottom-water conditions (energy and oxygen concentration), burial and sediment accumulation rates, and early diagenesis. Finally, this detailed study demonstrates that the down-dip distal organic carbon-rich lithofacies variations can be linked directly to the proximal up-dip lithofacies variability and there is no reason why these overall facies can't be combined under one overarching model as their deposition represents the same continuum of processes.

9.2. Recommendations for future research

This research was primarily motivated by the need to enhance our understanding of the conditions that controlled mudstone dispersal in ancient shelves and their modification during early burial. The detailed scope of this study and integration of the small-scale datasets have demonstrated that the existing models used to explain lithofacies variability underestimate the episodic character and dynamism of these systems. This section, however, seeks to provide some recommendation for future work that may develop the results of this research. Some specific points are presented below:

- This study has demonstrated that petrographic analyses (using optical and electron optical methods) are very important in obtaining detailed compositional and textual information about fine-grained sediments. These methods should be considered along with more conventional bulk rock analytical techniques in further similar studies.

- It is likely that the majority of mudstone-dominated successions will exhibit similar degrees of heterogeneity found here. Their deposition too is likely to have been highly dynamic and variable. To move our understanding of how these rocks formed studies that address the heterogeneity at small scales need to be adopted.

- To further our understanding of the processes responsible for organic carbon preservation it will be vital to integrate detailed geochemical analyses with knowledge of the scale of sediment heterogeneity. It is not reasonable to adopt traditional sampling strategies as so many genetic depositional units are sampled in these processes.

- In order to determine the facies variability on muddy continental shelves, additional work is needed to investigate the lateral lithofacies variability at different scales (1 to 10 m, 10 to 100 m, and 100 m to km).

- This study shows that the variability in production-dominated, organic-rich mudstones can be directly incorporated into basin-scale facies models, so additional detailed work is needed to define the sequence geometries that would confirm these interpretations.

- Finally, in order to understand the relative importance of mud-dispersal processes such as waves, tides, and storms in any mud-dominated succession, the characteristic microfabrics within this succession should be fully documented. Thus additional work to illustrate and compare all these microfabrics would be useful.

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