Diagenetic Modifications of The Eagle Ford Formation: Implications on Chemical and Physical Properties

A thesis submitted to the University of Manchester for the degree of Doctor of Philosophy in the Faculty of Science and Engineering.

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Diagenetic Modifications of the Eagle Ford Formation: Implications on Chemical and Physical Properties

Richard Thomas McAllister

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This thesis investigates the impacts of diagenesis on the Late-Cretaceous Eagle Ford Formation (Fmn) in south-west Texas. This was achieved utilising many techniques such as of outcrop and core analysis, standard petrographic techniques (including cathodoluminescence [CL] and scanning electron microscopy [SEM]), and geochemical analysis (x-ray diffraction [XRD], stable isotope analysis of C and O within inorganic minerals and Rock Eval pyrolysis). The bulk of diagenetic products and textures were identified via petrographic techniques, with geochemical analysis confirming interpretations based on visual observations.

This thesis shows the Eagle Ford Fmn is a calcareous, organic-rich mudstone containing eight distinct lithofacies, which have all been directly impacted by burial diagenesis. The Lower Eagle Ford Fmn mainly comprises of dark organic and clay-rich lithofacies which represent a classic source rock with interbedded carbonate rich lithofacies. The Upper Eagle Ford Fmn is organic and clay-poor, with the bulk of lithofacies carbonate dominated and heavily cemented. An initial anoxic, open marine depositional environment which transitions into an oxic deepening environment is inferred during deposition of the Eagle Ford Fmn.

Early, microbial derived redox reactions have precipitated authigenic calcite and pyrite within the Eagle Ford Fmn. Authigenic calcite infills and preserves biogenic debris (mainly planktonic and benthic foraminifera), with pyrite framboids post-dating the carbonate cements. Kaolinite infilling biogenic debris is also a common occurrence indicating it is also an early diagenetic product. Smectite is converted to mixed layer I/S and illite during deep burial processes at similar depths and temperatures to hydrocarbon generation and expulsion. Authigenic quartz cements precipitate within primary porosity and on top of carbonate cements. Chlorite is observed as the last mineral precipitated in the Eagle Ford Fmn, often pseudomorphed from kaolinite within the micritic matrix. Diagenesis has had the greatest impact on porosity distribution in the Eagle Ford Fmn. The organic, clay-rich lithofacies contain little intra/inter-crystalline porosity with the bulk observed as clay-held or organic porosity. Meanwhile the carbonate-rich lithofacies contain mainly intra-crystalline porosity.

Concretions are a common feature observed in the Lower Eagle Ford Fmn outcrops. Four concretion types were identified and studied using a variety of petrological and geochemical techniques. Diagenesis plays a major role in all concretions types. However, primary factors such as sea level fluctuation, sediment input and tectonic activity also have key impacts on the formation of concretions.
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Chapter 1: Introduction, Literature Review and Methodology
1.0 Introduction

Source rocks are now reservoirs. Due to the development and expansion of unconventional reservoirs in the last 5-10 years in the USA, oil & gas companies are now drilling directly into source rocks to produce economic quantities of hydrocarbons (Dubiel. R. F. et al., 2010, Dubiel et al., 2012, Donovan et al., 2012, Martin et al., 2011). Due to this sudden rush for “shale gas” (and oil), great scientific interest is being shown on fine grained, organic-rich siliciclastic rocks. Whether organic-lean, or organic-rich (the latter known as source rocks), mudstones, or “mudrocks” are poorly understood compared to their coarser grained siliciclastic relations (Taylor and Macquaker, 2014, Macquaker and Gawthorpe, 1993, Macquaker and Adams, 2003, Aplin and Macquaker, 2011, Aplin et al., 2006). This is largely due to sedimentary researchers in the past having a lack enthusiasm towards mudstones, due to their homogeneous appearance in outcrop and core. Their fine grained nature also deterred researchers due to the associated difficulties of examining fine grained materials with technology that was not sufficient to observe their composition and fabric easily (Macquaker and Adams, 2003, Macquaker et al., 2007). However, today with the development of electron microscopy techniques, high magnifications with clear contrasting images can be obtained with little effort. This allows the petrologist to obtain vital but basic information about mudstones, such as understanding their composition, physical and chemical properties (Adams and Mackenzie, 1998, Macquaker and Adams, 2003).

Not only were mudstones difficult to study for researchers and academics, but the hydrocarbon industry had little interest in them as reservoirs due to their “tight” characteristics, with porosity values between 1-10% and permeability values below 100mD (Yang and Aplin, 2009, Yang and Aplin, 2004, Aplin and Macquaker, 2011, Aplin and Larter, 2005). This makes the extraction of hydrocarbons notoriously difficult (Yang and Aplin, 2009). Therefore in the past, they were largely ignored by the petroleum industry in a production sense. Mudstones were seen as only a potential source or seal. Production focused entirely on conventional sandstone and carbonate reservoirs, such as the North Sea in northwest Europe, the Gulf of Mexico in the U.S, and the Arab States in the Middle East (Dubiel. R. F. et al., 2010, Dubiel et al., 2012). Because of this, little is understood regarding mudstones being reservoirs. With depleting conventional resources (such as the North Sea), the focus is shifting to other reserves. With the development of stimulation techniques using horizontal drilling and hydraulic fracturing (known as fracking),
exploration and production companies can now exploit the hydrocarbons (mainly gas) still present in the source rock, which have not been able to migrate during generation and expulsion (Dubiel. R. F. et al., 2010, Dubiel et al., 2012, Rahm, 2011, Davies et al., 2012).

In recent years, a substantial amount of research undertaken and published on mudstones has exclusively focused how these rocks were deposited and the subsequent environmental conditions which created them (Bohacs, 1998, Schieber, 1999, Macquaker et al., 2007, Macquaker and Jones, 2002, Macquaker and Adams, 2003, Donovan et al., 2012, Aplin and Macquaker, 2011). However, the diagenetic processes that mudstones undergo once deposited and buried are poorly understood and have had little attention paid to them (Schieber et al., 2000, Aplin et al., 2006, Bowman, 2010). Processes such as basin tectonics and thermal gradients during burial are known to have an influence on mudstone burial processes; however these are generally large scale processes and have little effect on mudstone diagenesis overall (Siever, 1983, Sheldon and Retallack, 2001, Curtis, 1977). Overall basin tectonics and thermal gradients affect smaller scale processes. It is the smaller scale processes, such as lithification and the precipitation of minerals that impose a direct influence on mudstone properties (Siever, 1983, Curtis, 1977). There are many diagenetic reactions which are known to be able to take place during mudstone diagenesis (Macquaker and Adams, 2003, Al Balushi et al., 2013, Thyberg and Jahren, 2011, Aplin and Taylor, 2013, Reinhard, 1986, Siever, 1983, Schmalz, 1967). Again, little is understood on the implications of these reactions and how they influence the properties mudstones acquire.

1.1 Aims

The main aim of this thesis is to build a better overall understanding of mudstone diagenesis and how diagenesis effects the physical (composition, fabric, porosity), and chemical (total organic content (TOC): hydrogen index: HI, stable isotope content), properties of the Eagle Ford Formation (Fmn), a mudstone unconventional reservoir in south-west Texas. The key objectives are:

1. To identify and describe the lithofacies present in the Eagle Ford Fmn.
2. Discuss and describe the depositional environments in which the Eagle Ford Fmn was deposited.

3. To identify the diagenetic processes that have occurred in the Eagle Ford Fmn and build a better overall understanding of mudstone diagenesis.

4. Investigate why concretions and laterally continuous limestone beds are present in the Lower Eagle Ford Fmn.

5. Discuss porosity types and their distribution between the lithofacies.

6. Discuss how all the above effects reservoir properties and where the best areas of the Eagle Ford ("sweetspots") are to target for stimulation and production.

All aims and objectives are addressed in the next five chapters of the thesis.

1.2 Material and Methods

1.2.1 Materials

Thin sections and geochemistry data (XRD, Rock Eval, stable isotope analysis) from 121 samples collected from wells; Lloyd Hurt 1, Shell J Hay E-D 1, Shell J A Leppard 1-H, Wagner Bros Inc 11, H-P Orts 2, was supplied by Statoil ASA, Norway at the start of the PhD. Statoil Gulf Services (US arm of Statoil ASA) have acreage in Karnes and Dewitt counties in south Texas and therefore have an economic interest in the Eagle Ford Fmn. The material from Statoil was obtained from exploratory cores slabbed at the Bureau of Economic Geology (BEG), Austin, Texas. These cores are open to public access (Figure 1.0).

Further data (38 thin sections accompanied with XRD analysis) obtained during the PhD from the Matthews J L 1-1, Shell J A Leppard 1-H, Shell J Hay E-D 1, J W Blumberg and W Bretchell BEG cores, when they were logged and sampled. Additional material (24 rock samples which created a further 34 thin sections, accompanying XRD and isotope data) was collected from outcrops/road cuts in west Texas during two field seasons in 2013 and 2015.
1.2.2 Methods

All analytical techniques performed on the material collected during the project was undertaken at the University of Manchester, with the exception of the Rock Eval pyrolysis and He porosimetry, which was performed by Statoil ASA in Bergen. Stable isotope analysis, was carried out at the University of Liverpool. Standard petrographic techniques including optical microscopy, cathodoluminescence (CL) and electron microscopy (SEM) forms the base of this project and was performed on thinly cut (20µm), highly polished thin sections. X-ray diffraction (XRD) was also undertaken at the University of Manchester.

Petrographic analysis

Thin sections were prepared at Statoil ASA, Bergen. All thin sections were scanned using a flatbed scanner (Cannon CanoScan 5600F), generating high quality whole thin section images. Each thin section was then analysed under low to medium resolutions ($10^{-3}$ to $10^{-4}$ m scale) under transmitted light (TL) in both plane polarised light (PPL) and cross polarised light (XPL) using a Nikon Optiphot2-Pol petrographic microscope. Examination of the thin sections under XPL was of little help due to the nature of high interference colours when the thin section is cut too thin. On top of the microscope viewing the thin sections was a Jenoptik jena-07739 digital camera allowing photomicrographs to be taken. A CITL Cathodoluminescence Unit (Model CCL 8200 mk3) was used alongside an Olympus BH-2 petrographic microscope, with both utilising a digital camera (Jenoptik jena-07739) to capture micrographs in CL and PPL. Operating conditions for the CL were approximately 20kv (cathode voltage), 300 µA electron beam current and 0.2 torr vacuum.

Petrographic, diagenetic and compositional information were obtained from these techniques. After TL and CL investigations 15 of thin sections were selected and carbon coated for electron optical analysis to examine the, composition and diagenetic fabrics and other constitutes at higher resolution ($10^{-5}$ to $10^{-6}$ m scale). A JEOL 6400 scanning electron microscope (SEM) with a solid-state, Link Systems 4-quadrant backscattered (BSE) detector was used to analyse the thin sections. Operating conditions for the SEM were 20kv, 2nA and a 15mm working distance. BSE micrographs were recorded and projected by a Semiwave digital framestore installed into the SEM. A semi-quantitative, energy dispersive X-ray system determined major element compositions of minerals (Fe, Si, Ca,
Identifying mineral composition was crucial to discriminate and geochemically quantify diagenetic phases of carbonate and other minerals.

**Mineralogical and geochemical analysis**

Qualitative and qualitative mineral composition of the Eagle Ford Fmn was determined by bulk samples, which were analysed by a X-ray diffractometer (XRD). A Philips PW1730 X-ray diffractometer (Cu Ka radiation) analysed the samples operating a tube voltage of 40 kV and a tube current of 20mA, a step size of 0.01° and a time constant of 2s. For each sample, a smear was prepared by mixing 0.5g of the sample with two drops of amyl acetate and leaving it to dry on a glass slide. Once dried the slide was placed into the XRD. Semi-quantitative estimations of bulk-mineralogy fractions were carried out using peak area measurements. To establish a better understanding of mineral composition (quantification), further analysis was conducted using the program TOPAS developed by Bruker. TOPAS is a quantitative program that analyses the peak areas but factors in the diffraction coefficients of the elements identified. The pattern fitting of the peaks and coefficients in TOPAS was good for the Eagle Ford Fmn samples so the mineral quantities should be close to reality, however there are limitations when compositions are < 2% . A hand-held XRF was also used to help determine the elemental composition of some of the samples collected in outcrop.

Stable carbon and oxygen isotope analysis was performed on the same (whole rock) 40 samples that were analysed by XRD. All 40 samples were subject to a cold methanol:dichloromethane (1:9 solvent) extraction at room temperature using an ultrasonic water bath to remove the organic content. To separate the sample and solvent they were centrifuged and then left in a fume cupboard over night to dry and let any excess solvent to evaporate. The samples were inserted into a VG SIRA-12; gas sourced mass spectrometer (MS) in the University of Liverpool Stable Isotope Laboratory, UK. Here, $^{13}$C/$^{12}$C and $^{18}$O/$^{16}$O ratios were measured. All results and ratios are presented by the standard delta ($\delta$) as parts per mill (‰) from the Vienna Pee Dee Belemnite (VPDB) international standard.

**1.3 Literature Review**

1.3.1 The Study Area: The Eagle Ford Formation (Fmn)
For this section and the rest of the thesis, the Eagle Ford Formation will be referred to as the Eagle Ford Fmn.

The Eagle Ford Fmn is a shale gas and oil reservoir in southern Texas, USA (figure 1.0). The formation was one of the later developed reservoirs during the shale gas boom in the USA (Driskell et al., 2012, Dubiel. R. F. et al., 2010, Dubiel et al., 2012). The Eagle Ford Fmn was drilled horizontally in 2008 by PetroHawk, a small independent drilling company who were the first to explore the formation for the possibility of shale gas via hydraulic fracturing, (Treadgold et al., 2011, Driskell et al., 2012, Walls and Sinclair, 2011). PetroHawk discovered and recovered a significant amount of gas with smaller quantities of oil, which opened the flood gates for other companies to exploit the formation (Driskell et al., 2012). The Eagle Ford Fmn is now a real focal point for production companies due to the formations ability to produce liquids (Martin et al., 2011, Dubiel et al., 2012). Few shale formations in the U.S produce liquids, and with dwindling gas prices the hunt for oil is prevalent, making the Eagle Ford Fmn one of the most drilled formations in the USA (Dubiel. R. F. et al., 2010, Dubiel et al., 2012, Macquaker and Adams, 2003, Scott, 2004).

1.3.2 Geology of the Eagle Ford Formation

The Eagle Ford Fmn outcrops along a significant area of southern Texas from western Dallas County passing through the town of Eagle Ford, of which the formation is named after, heads south through Waco, Austin, and onto San Antonio (Dawson, 1997, Dawson and Almon, 2010). South of the outcrops the Eagle Ford Fmn sits in the sub-surface and continues with a 2° dip in a south easterly direction, where at depths of ~7000ft organic matter has matured and generated economic quantities of hydrocarbons, (Hsu and Nelson, 2002b, Liro et al., 1994).

Many of the geological features that were present during the deposition of the Eagle Ford Fmn are associated with tectonic features from the Carboniferous (figure 1.0) (Treadgold et al., 2011, Driskell et al., 2012). The most prominent features are the Ouachita structural front and San Marcos Arch. The Ouachita structural front is essentially the boundary where the Eagle Ford Fmn occurs in outcrop at the surface (Blakey, 2011, Treadgold et al., 2011). From here the formation extends in a southerly direction into the subsurface (figure 1.1). The San Marcos Arch separates the southern and western areas from the eastern area of the Eagle Ford Fmn in the subsurface, due to the thinning of the formation (to as little as 15m) as it scales the arch (Treadgold et al., 2011, Driskell et al., 2012).
East of the San Marcos Arch the Eagle Ford Fmn overlies the Woodbine sandstone with an unconformable basal contact (Surles 1987; Liro 1994: Robison 1997)(Dawson, 1997). West and south of the San Marcos Arch the Buda Limestone underlies the Eagle Ford Fmn with an unconformable sharp contact (Robison, 1997, Surles, 1987). Both the Buda limestone and Woodbine sandstone are significant sedimentary units deposited during the mid- Cretaceous (figure 1.0) (Liro et al., 1994, Robison, 1997).

The Eagle Ford Fmn is an argillaceous sedimentary unit with its main detrital components supplied from the interior, via the Woodbine Delta (figure 1.0). The formation was deposited in the south-eastern sector of the Western Interior Seaway (WIS), which split North America during the Late Cretaceous (Surles, 1987, Hsu and Nelson, 2002b), (figure 1.0). The southern extent of the WIS flowed over the Edwards’s shelf edge and over the continental margin into the Maverick basin depositing significant quantities of sediment, some of which formed the Eagle Ford Fmn. The centre of the Maverick Basin at present is of most interest to drilling companies due to the thickness and maturity and at depths of >7000ft (Driskell et al., 2012, Donovan et al., 2012).
In the subsurface the Eagle Ford Fmn is split into two distinctive sections, the Lower Eagle Ford Fmn and Upper Eagle Ford Fmn (figure 1.0). At approximately 150m thick the Lower Eagle Ford Fmn section represents a typical laminated mudstone with a brown to black colour; while the Upper Eagle Ford Fmn Section is dark grey to light grey, usually heavily cemented and carbonate rich (Surles, 1987, Liro et al., 1994, Hsu and Nelson, 2002b). The Lower Eagle Ford Fmn has been interpreted to represent a transgressive systems tract, in warm open seas where, high quantities of organic matter are able to be preserved in anoxic environments (Pederson and Calvert, 1990, Tyson, 2005, Wignall, 1994). The Upper Eagle Ford Fmn has been interpreted by authors to represent a highstand and regressive systems tract. Here more carbonate is deposited (Liro et al., 1994, Surles, 1987). The Upper Eagle Ford Fmn still contains some dark units, however it mainly consists of interstratified grey wackestones and packstones, bentonites and limestone beds giving it a light grey colour compared to the Lower Eagle Ford Fmn (Surles, 1987, Liro et al., 1994). Mineral content can vary dramatically between the two sections but the average composition of the Eagle Ford is; Calcite ~50%, quartz ~20%, clay ~20% and kerogen ~10%. The Upper Eagle Ford Fmn has been interpreted to be deposited in a shallower marine environment compared to the Lower Eagle Ford Fmn (Driskell et al., 2012, Dubiel. R. F. et al., 2010, Donovan et al., 2012, Liro et al., 1994). However more recent studies dispute this statement. Deeper water environments are thought to have created the Upper Eagle Ford Fmn (Lowery et al., 2014, Corbett and Watkins, 2013).
1.3.3. Depositional Environments

Depositional environments and processes which created the Eagle Ford Fmn are still poorly understood. The Lower Eagle Ford Fmn, like other typical organic rich source rocks, is thought to be deposited in deep, distal marine waters with high levels of surface water primary production with an oxygen minimum zone and/or an anoxic zone at the sediment water interface (Pederson and Calvert, 1990, Arthur and Sageman, 2004, Monroe and Wicander, 2009, Tyson, 2005, Dawson and Almon, 2010, Dawson, 1997, Liro et al., 1994, Donovan et al., 2012, Driskell et al., 2012, Hsu and Nelson, 2002b, Lock and Peschier, 2006, Lock et al., 2010, Harbor, 2011, Robison, 1997, Creaney and Passey, 1993). Dissolved oxygen content in the oceans is considerably less during ocean anoxic events (OAEs) compared to today and other periods of earth’s history. It is suggested dissolved oxygen only penetrated the surface (trophic level) waters leaving the bottom waters inhabitable for most marine fauna during OAEs (Pederson and Calvert, 1990, Tyson, 2005). During the Late Cretaceous, specifically at the Cenomanian-Turonian boundary, ocean anoxia was particularly prevalent (OAE2), with oxygen minimum zones present across the world’s oceans and seas (Tyson, 2005, Pederson and Calvert, 1990, Wignall, 1994). The preservation of organic matter at the sediment water interface was much greater during OAEs. Prolific petroleum source rocks across the world during the Late Cretaceous (La Luna Shale in Venezuela, Natih B in Oman and the Kazhdami in the Persian Gulf), were deposited during OAE2 (Ruofei et al., 2014). OAE2 is traceable in the rock record and denotes the Cenomanian to Turonian boundary (Schlanger and Jenkyns, 1976, Donovan et al., 2012, Pederson and Calvert, 1990). Not only is OAE2 traceable by the abundance of petroleum source rocks deposited worldwide during the Late Cretaceous, but also by the $\delta^{13}C$ isotope record. (Wignall, 1994, Schlanger and Jenkyns, 1976, Cetean et al., 2008). A positive shift of $\delta^{13}C$ from $\sim\delta^{13}C$ 28‰ to $\sim\delta^{13}C$ 23‰, marks the excursion of large volumes of organic carbon being sequestered into sediments, producing organic rich source rocks (Wignall, 1994, Schlanger and Jenkyns, 1976). The $\delta^{13}C$ excursion is present in the Eagle Ford Fmn (figure 1.1) however it does not correlate to the most organic rich section of the formation, which was thought to represent depositional conditions produced by OAE2. Donovan et al 2010, show how the $\delta^{13}C$ isotope curve, denoting the onset of OAE2, begins its excursion as TOC and HI values decrease (figure 1.1).
The δ\textsubscript{13}C excursion at Lozier Canyon is similar to what is seen in at the C/T boundary in Pueblo, Colorado. (Eagle Ford isotope curve from Donovan et al 2010. Pueblo curve from Kennedy et al 2005).

This suggests OAE2 occurred, after the best source rock material (high TOC and HI), had already been deposited in the southern Western Interior Seaway (WIS). When OAE2 took place, carbonate precipitation was the dominant depositional material producing low TOC, faunal rich carbonates containing minor clay minerals. Kennedy et al 2005, reported a similar trend in Pueblo, Colorado, in the Greenhorn Limestone, a stratigraphic equivalent formation to the Eagle Ford Fmn, deposited further north (Colorado) in the WIS (Kennedy et al., 2005). Here there is an identical shift of the δ\textsubscript{13}C towards a more positive signature denoting the onset of global, mass organic carbon preservation in sediments (Figure 1.1).
The implications of organic rich sediments deposited in the Eagle Ford Fmn before the onset of OAE2, suggests the environment was already ideal for organic carbon preservation. Conditions such as ocean stratification, is typically driven by thermal and salinity variations, which create layer like barriers that block oxygen and nutrient mixing within the water column (Arthur and Sageman, 2004, Blakey, 2011, Wignall, 1994, Martin et al., 2012). With the Eagle Ford Fmn situated approximately 30° N paleo latitude during the Late Cretaceous, evaporation would have made the saline influx from the Tethyan more dense (Blakey, 2011). Martin et al 2012 suggest an input of the dense Tethyan water mass created sufficient stratification of the water column to produce water anoxia around the Comanche platform and southern Western Interior Seaway. Primary productivity rates are unknown and difficult to determine for the southern Western Interior Seaway, however are thought to be relatively high (Pederson and Calvert, 1990, Elder and Kirkland, 1994). Upwelling must have taken place to bring nutrients to the photic zone creating sufficient productivity needed to create organic rich sediments. Rising sea levels associated with OAEs could have ended the trend of organic carbon preservation in the southern WIS (Corbett and Watkins, 2013, Lowery et al., 2014). We suggest transgression associated with OAE2 increased ocean circulation and turnover within the southern Western Interior Seaway, supplying sufficient oxygen to the water column. This reduced the basins ability to preserve of organic carbon. Corbett et al 2013 suggest, artic derived boreal waters were drawn south along the then wider and larger, WIS along the western coast. While Tethyan waters were still being drawn north along the eastern coast via the Gulf of Mexico. With increasing sea levels, the lighter, fresher boreal waters were able to spill over the Sligo and Edwards platforms onto the Comanche platform and split the denser Tethyan current creating turnover within the water column. The mixing of water masses was likely to oxygenate the bottom waters during transgression and bring oligotrophic conditions when Cretaceous sea level was nearing its highest (Martin et al., 2012, Corbett and Watkins, 2013, Lowery et al., 2014). This hypothesis is supported by Corbett et al 2013, who analysed the ecology of the Western Interior Seaway. Found at the southern tip of the seaway, sediments within the Eagle Ford Fmn representing OEA2 (δ 13C excursion) contained high quantities of benthic nanofossils, compared to planktonic fauna that thrive in oxygen depleted environments (Corbett and Watkins, 2013, Lowery et al., 2014). Extensive bioturbation present in the lower Turonian sediments, low TOC values and high carbonate content also suggests bottom water oxygenation. Donovan et al 2012 also state the same observation. The breaking down of ocean stratification and the oxygenation of
deeper waters prevented anoxia and weakened the basins ability to preserve organic carbon during OEA2 and thereafter.

1.3.4 Petrophysical properties and Geochemistry of the Eagle Ford Formation

The Eagle Ford Fmn is a typical tight mudstone with small porosity and permeability flows (Hsu and Nelson, 2002b). Porosities range between 3 and 10% due to varying quantities of siliceous and carbonate cements, with mean porosities 4-6% (Liro et al., 1994, Hsu and Nelson, 2002b). Permeability ranges from 3- 1000nd with a mean of 150-180nd (Hsu and Nelson, 2002b, Liro et al., 1994, Fishman et al., 2013b). TOC (weight%) content in the Eagle Ford ranges from 0.5 to 11% with the mean being around 4% for the entire formation (Robison, 1997, Liro et al., 1994). The Lower Eagle Ford Fmn contains the higher TOC% values and is renowned as the “source rock”. The Upper Eagle Ford Fmn contains lower values (1-3 TOC%). Geochemical analysis in the literature shows mainly type II kerogen with some type II/III and negligible type III present (Liro et al., 1994, Hsu and Nelson, 2002b, Dawson and Almon, 2010, Robison, 1997). As the Eagle Ford Fmn deepens (dips towards the south) towards the Gulf of Mexico the organic matter matures passing through the maturity phases: oil, gas condensate (gas/oil), and dry gas (Figure 1.3) (Treadgold et al., 2011, Driskell et al., 2012). The Maverick Basin contains some of the deepest sediments of the Eagle Ford where organic matter passes in into metagenesis and the carbon residue window (Driskell et al., 2012, Dubiel et al., 2012, Liro et al., 1994, Dawson and Almon, 2010).

The Eagle Ford Fmn is classified as a self-sourced petroleum system due to the source, reservoir and seals being present in the same unit. This is possible due to the low porosities and low permeability’s typical of mudstones (Liro et al., 1994, Hsu and Nelson, 2002b). However, the bulk of hydrocarbons have migrated to units stratigraphically above, such as the Austin Chalk and Wilcox formations (Dubiel. R. F. et al., 2010, Dubiel et al., 2012). Because the Eagle Ford Fmn has some porosity and permeability it is likely migrating hydrocarbons primarily moved along bedding planes during expulsion and migration (Liro et al., 1994, Dawson, 1997, Dawson and Almon, 2010). There are no conventional traps in the Eagle Ford. Hydrocarbons are likely to have migrated up dip (north) into shallower areas of the Eagle Ford and Austin Chalk. Bedding planes are extremely small and are essentially tiny microfractures between the shale laminations.
Figure 1.2 (modified from Driskell et al. 2012). Maturity phases in the Eagle For Fmn. Up dip where the formation is reaching sufficient temperature only oil is produced. As the formation is further buried in a southerly direction towards the Gulf of Mexico, temperatures increases and gas condensate then eventually dry gas are produced.

1.4 Diagenesis

Diagenesis is the physical, chemical or biological modification of sediment during, but mainly after deposition (Friedman, 1964, Lindgreen, 1988, Siever, 1983, Schmalz, 1967). These changes, or reactions, can happen at relatively low temperature (0-50°C) and pressures. Usually at these temperatures and pressures the mineralogy does not change, as does the matrix of the sediment (i.e. bonds are not broke between atoms). Diagenesis means “all the changes that occur in sediments and sedimentary rocks up to the time they enter the realm of metamorphism. Here rocks are getting close to the moho or certainly temperatures associated with the moho” (Munnecke et al., 1997).

Diagenesis of rocks proceeds under the influence of subcritical fluids; liquids and their associated vapour phases (Taylor and Macquaker, 2014, Munnecke et al., 1997, Laubach et al., 2010, Reinhard, 1986). Important consequences of the subcritical chemical behaviour
of diagenetic fluids include the fractionation of gases; CO₂, CH₄ and other light hydrocarbons, between the gas and liquid phase (i.e. dissolved gases). For example, the existence of a CO₂-H₂O un-mixing solvus controls the composition of the CO₂ bearing diagenetic solute that precipitates. Minerals precipitating from solution are the most important for the creation and destruction of subsurface porosity (Reinhard, 1986, Moore, 1989, Friedman and O'Neill, 1977, Friedman, 1964, Fein, 1994).

Lithification is also a form of diagenesis. Lithification is the process in which sediments compact as they are buried from overlying sedimentary units. Under pressure they expel fluids, mainly water and become solid rock. Lithification is a process of porosity reduction (destruction) through compaction and cementation (Fein, 1994, Bernaud et al., 2006, Cade and Gluyas, 1992, Oertel and Curtis, 1972). Lithification includes all the processes which convert unconsolidated sediments such as sands, mud, silt into solid sedimentary rocks, e.g. sandstone (Oertel and Curtis, 1972, Aplin et al., 2006).

Diagenesis can be split into three parts (Worden et al., 2000a, Worden et al., 2000b, Schmalz, 1967, Reinhard, 1986). The first is Eogenesis (early diagenesis), which involves changes that occur near the sedimentation surface where the interstitial solutions are still in communication with the overlying water mass. Mesogenetic (late diagenesis), meaning after burial, involves changes taking place when the pore filling solutions are sealed and are not in contact with the overlying water mass. Here sediments are renowned as mesogenetic. Most sediments stop in this realm through their history. Telogenetic diagenesis occurs under the direct influence of meteoric solutions following uplift and erosion (Worden et al., 2000a, Worden et al., 2000b, Schmalz, 1967, Reinhard, 1986). This is known as telogenetic because diagenetically modified sediments/rocks are likely to be stable in their mesogenetic state. However when they come into contact with a significant water body again they diagenetically modify a third time. Usually the waters they come into contact after uplift or erosion are of different mineral composition compared to the original waters they were deposited in (Worden et al., 2000a, Michalopoulos and Aller, 2004, Laubach et al., 2010, Heydari and Wade, 2002).

Constructive diagenesis tends to fill pore space of sandstones and carbonates by authogenic growth of one or more isochemical or allochemical minerals such are quartz, carbonate and/or anhydrite (cementation) (Worden et al., 2000a, Williams et al., 1985, Taylor et al., 2010, Schmalz, 1967). Mineral replacement can also occur. This is known as dissolution as
one mineral is replaced for the precipitation of another. This can happen on a volume to volume or molecule to molecule basis. This can happen in any of the three realms of diagenesis (Oertel and Curtis, 1972, Curtis, 1977, Sayles and Manheim, 1975, Reinhard, 1986, Heydari and Wade, 2002).

Destructive diagenesis, also known as ‘solution porosity’, relates to the decomposition of minerals in reservoir sandstones and carbonates or in claystones/mudstones (Yang and Aplin, 2009, Schieber et al., 2000, Peltonen et al., 2009, Aplin et al., 2006). With the removal of minerals and solutions porosity and sometimes permeability, increase. Recognition of this is partial dissolution, molds, unhomogeneity of packing and floating grains, oversized pores, elongated pores, corroded grain margins honeycombed grains and fractured grains (Yang and Aplin, 2009, Moore, 1989, Fein, 1994).

Temperature is a major factor of diagenesis (Worden et al., 2000a, Worden et al., 2000b, Nadeau et al., 1985, Heydari and Wade, 2002, Freed and Peacor, 1989). Average thermal gradients across the world is \(28^\circ\text{C}/1000\text{m}\) (Pepper and Corvit, 1995). Higher geothermal gradients can occur in sedimentary basins when they surround, or are surrounded by igneous intrusions. Here temperatures increase over shorter distances (depth) and can be more like \(50-80^\circ\text{C}/1000\text{m}\). In regions with higher geothermal gradients porosities in rocks are usually lower (Worden et al., 2000a, Worden et al., 2000b, Pepper and Corvit, 1995, Bowman, 2010).

Carbonate rocks all are mainly characterised by the depositional environment they are deposited in. Water depth, temperature profile, sediment input (inorganic/organic input), currents and tectonic uplift can all affect the diagenetic processes which create carbonate rocks (Taylor, 2010, Scott, 1993, Scholle and Ulmer-Scholle, 2003, Schmalz, 1967, Philip et al., 1995). These attributes affect the composition of the pore water which have an important part on how the rocks from beneath the surface. Not only do the mentioned attributes affect pore waters but also the CCD, lysocline and thermocline (Presley and Kaplan, 1968, Moore, 1989, Matthews, 1968, Kim and O'Neill, 1997, Irwin, 1977).

Volumetrically the most important solid materials for early diagenetic processes in muddy sediments are the finer mineral fractions of soils (Worden et al., 2000b, Taylor and Macquaker, 2011, Peltonen et al., 2009, Mondol et al., 2008, Curtis and Spears, 1968). All Fe bearing carbonates, sulphides and aluminosilicate minerals are very unstable relative to low soluble hydrated oxides of Fe\(^{\text{III}}\) in the presence of atmospheric \(\text{O}_2\) (Oertel and Curtis,
1972, Curtis and Spears, 1968, Curtis, 1977). HCO$_3^-$ and SO$_2^{4-}$ are the stable C and S species. These hydrated oxides (such as goethite FeO(OH) or ferrihydrate Fe(OH)$_3$) are dominant in soils and must be expected to account for the greater part of the Fe in mud’s of deposition (Oertel and Curtis, 1972, Macquaker et al., 1997, Curtis and Spears, 1968). Yet they are rarely reported in recent sediment studies and almost never so in ancient mudstones. The implication is obviously that redox reactions involving Fe are fast and play a very important part during early diagenesis (Taylor and Macquaker, 2011, Oertel and Curtis, 1972, Macquaker et al., 1997, Curtis, 1977, Canfield et al., 1992, Canfield, 1989).

1.4.1 Diagenetic pathways in mudstones

It was thought mudstones were mainly made of detrital material and their characteristics were defined by their fine (<62.5µm) detrital composition (Mondol et al., 2008, Laubach et al., 2010, Ajdukiewicz et al., 2010, Thyberg and Jahren, 2011) However past and more recent research (Thyberg et al., 2010, Thyberg and Jahren, 2011, Taylor, 2010, Oertel and Curtis, 1972, Curtis and Spears, 1968, Curtis, 1977, Reinhard, 1986, Sayles and Manheim, 1975), suggest diagenetic reactions during burial have a significant factor on controlling mudstone composition, and in fact most of the composition can be of authigenic origin. Focus in industry and academia has now turned to diagenesis and how this effects the composition of mudstones (Taylor and Macquaker, 2014, Macquaker et al., 2014, Rine et al., 2013, Bust et al., 2013, Al Balushi et al., 2013). It has been suggested that mudstones in particular due to their natural reactivity, go through such diagenetic modification that little of what was originally deposited at the sediment-water interface is present at depth in its original state (Thyberg et al., 2010, Thyberg and Jahren, 2011, Curtis, 1977, Worden et al., 2000b, Taylor et al., 2010).

Schmalz 1967 and Lindgreen 1988 describe how diagenesis begins immediately during deposition at the sediment-water interface in mudstones with processes such as; lithification, pore water expulsion, organic matter oxidation and the precipitation and dissolution of minerals, which can continue throughout till metamorphism deep in the earth’s crust (Friedman, 1964, Schmalz, 1967) (Coleman, 1985, Coleman and Raiswell, 1995).
Compaction of mudstones expels large amounts of water. (Siever, 1983, Laubach et al., 2010, Claypool, 1974). Some clay minerals may also act as catalysts for the transformation of organic matter into hydrocarbons (Worden et al., 2000b, Nadeau et al., 1985, Mondol et al., 2008, Burton et al., 1987, Bethke et al., 1986). Mudstones are usually highly reactive as they tend to consist of a lot of clay due to their octahedral and tetrahedral sheets. Pore fluids react with clay particles and precipitate new minerals, or cause dissolution of already present minerals. (Peltonen et al., 2009, Oertel and Curtis, 1972, Nadeau et al., 1985).

Diagenesis of organic matter (OM) is mainly biological during the early stages of burial, as well as temperature and pressure driven at a later stage (metagenesis) (Curtis et al., 2011, Curtis, 1977, Pepper and Corvit, 1995). Mudstones are likely to carry pore waters with higher loads of bicarbonate compared to sandstones. OM-rich muds will have pore solutions rich in $\text{HCO}_3^-$ and metals. Cementation is likely to occur due to the bicarbonates available to feed reactions. Most common products of early diagenesis are:

- $\text{FeS}_2$- pyrite,
- $\text{FeCO}_3^-$ siderite,
- $\text{CaCO}_3$- calcite,
- $\text{CaMg(CO}_3)_2$- dolomite,
- all with some concentration of magnesium, ferroan and mangunoan substitutions. Some aluminosilicates (or their precursors) also form very early, notably: bertherine (Fe, Mg, Al $[\text{Si}_2 \text{ Al}_3 \text{ O}_{20}]$ (OH$_{16}$)). Glauconite $\text{K}_{1.5}(\text{Fe, Al})_4[\text{Si}_{6.5} \text{ Al}_{1.5} \text{ O}_{20}]$ (OH$_4$). Kaolinite $\text{Al}_2\text{Si}_2\text{O}_5$(OH)$_4$ (Worden et al., 2000a, Worden et al., 2000b, Williams et al., 1985, Taylor et al., 2010, Schmalz, 1967, Peltonen et al., 2009, Curtis and Spears, 1968, Curtis, 1977).

Diagenetic modifications can occur at low temperatures in mudstones, such as at the bottom of deep water bodies where temperatures are no more than 4 or 5°C. However they range from such low temperatures to temperatures as high at 300°C deep in the earth’s crust as the realm of metamorphism (Schmalz, 1967, Siever, 1983, Astin and Scotchman, 1988, Scotchman et al., 2000). At low temperature and pressures (assuming on the surface or not far under the surface) the overall matrix of the sediment is not altered, i.e. bonds are not broken between atoms (Friedman, 1964, Schmalz, 1967, Siever, 1983, Aagaard and Jahren, 2010). As temperatures and pressures increase bonds between atoms are destroyed and the rock composition begins to deform with new minerals being precipitated along the way. This is lithification (Friedman, 1964, Schmalz, 1967, Siever, 1983, Aagaard and Jahren, 2010).

Friedman 1964, identified lithification as one of first diagenetic processes in mudstones due to mud’s ability to be compacted easily. This caused the expulsion of water which is
Lithification is a porosity reduction process closing pores within the rock (Laubach et al., 2010, Friedman, 1964). This is the first and one of the main steps for porosity and permeability reduction in mudstones (Aagaard and Jahren, 2010). Generally porosity and permeability will decrease as burial depths increase (Figure 1.3) (Aagaard and Jahren, 2010, Worden et al., 2000b, Reinhard, 1986, Laubach et al., 2010). However, early diagenetic processes such as the precipitation of carbonate cements, can retard compaction as they fill pores and stop them collapsing during lithification (Aagaard and Jahren, 2010, Aplin et al., 2006, Al Balushi et al., 2013). Pore waters from mudstones contain high quantities of heavy metals, bicarbonate and other reactive solutions, which can be either highly alkaline or acidic. These solutions can be in either gas or liquid phase and are key for the dissolution and precipitation of cements in mudstones, (Bathurst, 1974, Laubach et al., 2010).

Aagaard and Jahren (2010) found cements have a detrimental effect on mudstone characterisation. Cements can re-enforce the mud/clay matrix and essentially hold pores and fractures open helping to preserve porosity and permeability (Aagaard and Jahren, 2010). On the other hand cements can precipitate in fractures and fill them closing porosity and permeability (Aagaard and Jahren, 2010). In most circumstances, mudstone cements close pores and restrict permeability (Aagaard and Jahren, 2010, Aplin and Larter, 2005).

1.4.2 Early diagenesis-microbial derived diagenesis

Many early diagenetic processes are triggered by microbial mediated redox reactions. The earliest reactions are redox reactions involving O, Fe, Mn, C and S. These elements feature prominently in the earliest diagenetic minerals (Oertel and Curtis, 1972, Curtis and Spears, 1968, Curtis, 1977, Raiswell, 1988, Al Balushi et al., 2013). Overall mineralogy, chemical and isotopic compositions of sulphate, carbonate, are all markers which record interactions of provenance (source, catchment, climate), depositional environment (marine, freshwater, evaporitic lake) and rate of sediment accumulation (Worden et al., 2000a, Worden et al., 2000b, Schmalz, 1967, Reinhard, 1986, Mackin and Aller, 1984b, Lindgreen, 1988, Bathurst, 1974). Sedimentation rates are important as they determine mineral composition,
assemblages and biogeochemical zones in the water column (Yamaguchi et al., 2010, Worden et al., 2000a, Reinhard, 1986).

Curtis 1977 discovered microbial activity as one of the main catalysts for diagenetic processes during early diagenesis as temperatures are ideal for microbes to flourish (Berner and Faber, 1996, Curtis, 1977). Organic matter decay can occur from 0-200m depth; beyond 200m tends to be too hot for organisms to survive (Berner and Faber, 1996). However, before sediments settle on the seabed modifications to organic matter can be taking place in the water column (Yamaguchi et al., 2010, Silva and Duarte, 2015, Mackin and Aller, 1984b, Barcelona, 1980).

Claypool (1974), suggested that diagenetic modifications of organic matter are mainly biological, active at an early stage of burial and can take place within the water column when organic matter is falling from the surface waters (Yamaguchi et al., 2010, Claypool, 1974, Tyson, 2005). Oceanographers and geochemists have identified biogeochemical zones, such as surface waters, the phototactic zone, oxic, suboxic, and anoxic zones where certain reactions predominate (Tyson, 2005). Aerobic microorganisms in the uppermost sediment layer and water column consume free oxygen and degrade organic matter (Claypool, 1974, Tyson, 2005). Organic matter is the first compound to be degraded by microbes as it has the lowest activation energy and gives the largest unit energy per mol (Schmalz, 1967, Siever, 1983). Organic matter oxidised to CO$_2$ in oxygenated zones is completely destroyed (Friedman, 1964).

Pederson 1990, Wignall 1994 & Tyson 2005 put forward that in anoxic environments anaerobic bacteria reduce organic matter to CO$_2$, ammonia and H$_2$O. During this reaction reaction potential (Eh) abruptly decreases and the pH increases. Sulphate is converted to sulphide (H$_2$S, HS$^-$) and may be bound to organic matter if iron is in little abundance (Matthews, 1968, Taylor and Macquaker, 2011, Taylor and Macquaker, 2014, Macquaker et al., 2014, Aplin and Taylor, 2013). This is common in marine type II kerogens, (Wignall, 1994). Hydrated oxides of Manganese and Iron are reduced to soluble Mn$_2^+$ and Fe$_2^+$ by bacteria and create carbonates and hydroxides.

Oceanographers and geochemists have also identified biogeochemical zones at the sediment water interface and first few metres of sediment (Macquaker et al., 1997, Curtis, 1977, Yamaguchi et al., 2010). Within each zone certain redox reactions predominate. Organic matter is aerobically oxidised to CO$_2$ and H$_2$O in the oxic zone (when oxygen is
available) (Yamaguchi et al., 2010, Tyson, 2005, Pederson and Calvert, 1990, Creaney and Passey, 1993). If oxygen is present aerobic oxidation of organic material can occur in the water column, on the sediment water interface, or first few mm of sediments. In aerobic environments, O$_2$ acts as the electron acceptor (Yamaguchi et al., 2010, Pederson and Calvert, 1990, Curtis, 1977). Beneath the 2-5cm of sediment where oxygen is generally not available, or O$_2$ has been used up, various positively charged atoms serve as electron acceptors. This is the anoxic zone (Curtis, 1977, Yamaguchi et al., 2010, Worden et al., 2000b, Reinhard, 1986, Laubach et al., 2010, Friedman, 1964, Al Balushi et al., 2013). Anaerobic reactions are almost always bacterially mediated, rather than abiotic. Bacteria as a group use the most energetically favourable reaction, and some individual species can use different reactions depending on the most energetically favourable electron acceptor available (Yamaguchi et al., 2010, Williams et al., 1985, Sayles and Manheim, 1975, Reinhard, 1986, Friedman, 1964, Bathurst, 1974). Thus, natural systems use the reactions below in a progression from 1 to 6 with methanogenesis in effect the reaction of last resort.

Simplified redox reactions during early diagenesis:

1) Aerobic oxidation, CH$_2$O + O$_2$ = CO$_2$ + H$_2$O
2) Nitrogen reduction, 5CH$_2$O + 4NO$_3^-$ + 4HCO$_3^-$ + 2N$_2$ + CO$_2$ + 3H$_2$O
3) Iron reduction (FeR) 2Fe$_2$O$_3$ + CH$_2$O + 3H$_2$O = 4Fe$^{2+}$ + HCO$_3^-$ + 7OH$^-$
4) Manganese reduction (MnR), 2MnO$_2$ + CH$_2$O + H$_2$O = 2Mn$^{2+}$ + HCO$_3^-$ + 3OH$^-$
5) Sulphate reduction (SR), 2CH$_2$O + SO$_4^{2-}$ = HS$^-$ + H$^+$ + 2HCO$_3^-$
6) Microbial Methanogenesis (ME), 2CH$_2$O + H$_2$O = CH$_4$ + H$^+$ + HCO$_3^-$

The above reactions may occur separately or together and they may vary in terms of lateral and vertical extent. Therefore the patterns of zonation are complex and variable (Friedman and O'Neill, 1977, Friedman, 1964, Curtis, 1977). In reactions 2-5, the $\delta^{13}$C composition of carbonate (HCO$_3^-$) precipitated can indicate which reaction has taken place (Clayton, 1991, Irwin, 1977, Arthur and Anderson, 1983, Anderson and Arthur, 1983). Organic matter in reactions 1-5 stays isotopically preserved despite being degraded, ($\delta^{13}$C = -20/-30‰ VPDB). Carbonate derived from microbial methanogenesis is isotopically heavier, ($\delta^{13}$C = +10 to +20‰)(Clayton, 1991). $^{12}$C is easier for microbes to consume compared to 13C, so methane is preferentially enriched with $^{12}$C (biogenic methane -80-90‰VPDB)(Schmalz, 1967, Clayton, 1991, Coleman, 1993, Coleman and Raiswell, 1993).
Marine derived limestones have an isotopic composition ≈ 0‰ VPDB. Carbonate within mudstones can vary from -22.7‰ to +7.7‰ (Scotchman et al., 2000, Scotchman, 1991, Scotchman, 1989, Schmalz, 1967, Moore, 1989). This variation in carbonate isotopic composition indicates the variation of microbial processes undertaken by mudstones and provides evidence that the production of carbonate occurs at shallow burial depths, where pore waters are still in contact with the sediment-water interface, (Oertel and Curtis, 1972, Curtis, 1977, Presley and Kaplan, 1968, Taylor and Macquaker, 2014, Macquaker et al., 2014).

Macquaker 1997 identified two key diagenetic pathways in typical shelf mudstones (Aplin and Macquaker, 2011, Macquaker and Jones, 2002, Macquaker et al., 1997). In clastic iron rich muds, sulphate and iron reduction is prevalent due to the high input of iron oxides from terrestrial sources. Here the following sulphur and iron reduction reactions occur (Macquaker et al., 1997);

\[
\begin{align*}
SO_4^{2-} + 2CH_2O &= 2HCO_3^- + HS^- + H^+ \\
2Fe_2O_3 + CH_2O + 3H_2O &= HCO_3^- + 4Fe^{++} + 7OH^- \\
HS^- &= sulphide, 2Fe_2O_3 = iron oxide, HCO_3^- = carbonate (cement), 4Fe^{++} = ferrous iron, 7OH^- = carboxyl group-alkaline.
\end{align*}
\]

The resulting sulphide and iron (II) means pyrite becomes a dominant diagenetic phase as sulphur is sequestered into the iron creating pyrite and not organic matter, (Macquaker et al., 1997, Oertel and Curtis, 1972, Curtis and Spears, 1968). Matthews 1968 found the reduction of iron produces the resulting bicarbonate and alkalinity, which leads to carbonate precipitation and the cementation of mudstones, (Macquaker et al., 1997, Aplin and Macquaker, 2011, Matthews, 1968, Taylor, 2010). When iron oxides are abundant and sulphate is scarce, iron reduction can dominate the diagenetic pathway. Iron reduction can be the only reaction which takes place. No pyrite is produced as there is no sulphur present (Macquaker and Adams, 2003, Taylor and Macquaker, 2011, Aplin and Taylor, 2013). In iron depleted systems where terrestrial input is minimal, sulphur reduction is the main diagenetic reaction (Macquaker et al., 1997). In these systems sulphate reduction and subsequent sulphide oxidation lower the pore water pH. As there is no iron present sulphur can be incorporated into the organic matter (kerogen) (Pepper and Corvit, 1995). The following reactions occur;
SO$_2^-$ + 2CH$_2$O = 2HCO$_3^-$ + HS$^-$ + H$^+$

H$_2$S$^-$ + 2O$_2$ = SO$_4^{2-}$ + H$^+$

H$_2$S is incorporated into the kerogen, which causes issues for the petroleum industry, as H$_2$S is highly poisonous and corrosive (Macquaker et al., 1997, Canfield et al., 1992). However it can be recycled by microbes to produce sulphate, which acidify the pore waters within mudstones and dissolve carbonate rocks and cements (Macquaker et al., 1997, Canfield et al., 1992). In iron-depleted environments, the precipitation of phosphate cements is common. (Macquaker et al., 1997, Canfield et al., 1992, Curtis, 1977, Taylor and Macquaker, 2011, Macquaker et al., 2014).

Sayles & Manheim (1975), discovered pore waters from DSDP cores from around the world’s oceans showed systematic changes in pore water composition only a few metres below the sediment-water interface. Sulphate depletion was almost present in all cores and complete in nearly all cores which represented rapidly deposited terrigenous sediments. Along with sulphate reduction, Sayles & Manheim 1975 also found the enrichment of bicarbonate and ammonia due to the breakdown of organic matter.

Matthews (1968), Presley & Kaplan (1968), Claypool & Kaplan (1974), Sayles & Manheim (1975), all suggested that carbonates produced where bacterial activity is less prominent; were found to be likely locations for recrystallisation and precipitation of various carbonate minerals at relatively shallow depths. Biogenic carbonates were found to recrystallise, especially high magnesium calcite and aragonite carbonates with the precipitation of dolomite at shallow depths.

Reduced iron minerals as sulphides and low concentration ferrous iron in the sulphate reduction zone form iron poor carbonates such as calcite and dolomite (Macquaker et al., 1997, Canfield et al., 1992). In the iron reduction zone, iron rich carbonates can precipitate, but low iron content minerals are still more common (Macquaker et al., 1997, Taylor and Macquaker, 2011, Taylor and Macquaker, 2014). There is little doubt that during low burial diagenesis biological processes driven by bacteria have a significant impact on the assemblage of rocks, minerals and the alteration of organic matter (Taylor et al., 2010, Macquaker and Adams, 2003, Macquaker and Jones, 2002, Macquaker et al., 1997). The most important of these processes is the production of sulphide and carbonates and phosphate precipitation. However bacteria driven aside, Reinhard 1986 &
Singleton 2002 argue that the interaction of pore waters with the sediment water interface and even meteorological water are an important element of shallow burial diagenesis. The interaction of pore water shapes the organic and inorganic compounds which occur in shallow deposited sediments (Reinhard, 1986, Singleton et al., 2002).

Studies by Macquaker (1997, 2002), show that iron reduction continues into deep burial. This is based on the decreasing fraction of iron found in sediments with increasing depth. The fact that iron is present at all shows that iron reduction continues to higher depths because iron minerals can still precipitate. This is important because a metal cation could be produced for carbonate precipitation (or other minerals). Also it is important because the iron reduction reaction must be accompanied by an equivalent oxidation reaction (reducing agent). At depths over 100m only one agent is available- organic matter. The reaction is;

$$2\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O} + \text{CH}_2\text{O} = 4\text{Fe}^{2+} + \text{HCO}_3^- + 7\text{OH}^-$$

This reaction and others similar to it would modify organic matter but not in a way that is seen in shallow burial environments (Taylor and Macquaker, 2011, Macquaker et al., 1997). This reaction creates a high alkaline environment that would allow the precipitation of carbonate cements from the pore waters at higher temperature and pressures (figure 1.4) (Macquaker et al., 1997, Lindgreen, 1988). This process is likely to be a second phase of cementation in mudstones during burial diagenesis (Lindgreen, 1988, Al Balushi et al., 2013, Laubach et al., 2010, Arugundade and Sohrabi, 2012, Thyberg and Jahren, 2011).

Numerous authors, Claypool & Kaplan 1974, Curtis 1977, Sayles & Manheim 1975, Presley Kaplan 1968 Macquaker 1997, 2002, and many others, have shown through various studies using different techniques that diagenetic processes in the first few metres of clay marine sediment are bacterial driven (figure 1.4). When organic matter is present, which is nearly always in varying quantities, bacteria thrive and produce reactants and minerals. Bacteria utilising oxygen close to the sediment-water interface, sulphate reducing bacteria and fermentation bacteria all produce bicarbonate, which are transformed into diagenetic carbonates such as; calcite, dolomite, ankerite and siderite. Claypool 1974 conclude that methane produced from microbial methogenesis (if present), is consumed in the sulphate reduction zone of marine sediments and can be consumed while methanogenesis is taking place at the same time. This is described as a commensal relation between the two sets of bacteria. As one produces methane the other consumes it to reduce
sulphur. From their results they found in the Santa Barbara basin off the southern coast of California that the sulphate reduction zone was in the first 2-3m of sediment below the sediment-water interface. Between 1.75 and 3.25m there was a clear increase in methane concentration in the sediment suggesting that sulphate reduction was less prominent with increasing depth. Claypool 1974, conclude that methanogenesis continues throughout marine sediments to some considerable depth (>50 but <100m). As methane travels to the surface it is consumed in the first few metres below the sediment-water interface.

However, Reinhard 1986 & Singleton 2002 conclude little is still known about certain aspects of shallow diagenesis. One aspect in particular is what happens to amorphous material. Little is known about the processes clays undergo before transforming into mudstones.

![Diagram of diagenetic zones in mudstones and the common minerals they precipitate. Note average thermal gradient of 27.5°C/km. Figure from Curtis (1977)](image)

**1.4.3 Late diagenesis and clay mineral diagenesis**

Ortel (1972), explains how clay fabrics undergo modifications during burial. When clay is deposited in a marine environment, porosity values <10m of depth are in excess of 50%
Clay minerals are orientated in random positions due to ‘face-edge’ electrostatic interactions. During compaction the increasing strain from the overburden above overcomes the electrostatic interactions forcing the clay grains towards the horizontal (Aplin and Taylor, 2013, Aplin et al., 2006, Aplin and Larter, 2005, Aplin, 2000).

Little is understood on overall clay mineral diagenesis in mudstones (Taylor and Macquaker, 2014, Macquaker et al., 2014, Aplin and Macquaker, 2011). Bar the alignment of clay grains due to compaction, de-watering during lithification, little is known until clays reach depths where sufficient temperatures allow the smectite-illite reaction to occur (Worden et al., 2000b, Niu et al., 2000, Mondol et al., 2008, Leo Lynch, 1997, Burton et al., 1987). Mixed layer illite/smectite (I/S) is a common authigenic interstratified clay mineral composed of illite and smectite layers arranged in a stacking sequence along the crystallographic c* axis (Worden et al., 2000b, Leo Lynch, 1997, Freed and Peacor, 1989, Burton et al., 1987, Bethke et al., 1986, Aplin et al., 2006). Smectite and illite are often the main clay minerals in marine mudstones, which are sourced from terrestrial soils and rock formations on the continent, but diagenetically modified during burial. Smectite differs to illite due to smaller negative charges on silicate sheets, the presence of water and interchangeable cations of interlayer positions, and its ability to expand to water and organic solvents (Niu et al., 2000, Mondol et al., 2008, Leo Lynch, 1997, Freed and Peacor, 1989, Aplin et al., 2006). Mixed layer I/S can vary in composition due to the amount of illite interlayered within smectite, and the arrangement of the layers within stacking sequences themselves (Mondol et al., 2008, Freed and Peacor, 1989, Bethke et al., 1986, Nadeau et al., 1985, Peltonen et al., 2009). Many clay researchers have observed that ratio of I/S in mudstones becomes progressively larger with depth, with 70-80% illite marking the completion of the conversion reaction (Worden et al., 2000b, Taylor and Macquaker, 2014, Peltonen et al., 2009, Oertel and Curtis, 1972, Niu et al., 2000, Nadeau et al., 1985, Mondol et al., 2008, Freed and Peacor, 1989, Boles and Franks, 1979, Bethke et al., 1986, Aplin et al., 2006). Due to the water content difference between the two and increased interlaying, illitisation effectively makes the mixed layer I/S denser. This smectite-illite transition reaction, creating mixed later I/S occurs at similar temperatures to hydrocarbon generation (80-100°C) (Oertel and Curtis 1972, Boles and Franks 1979, Nadeau, Wilson et al. 1985, Bethke, Vergo et al. 1986, Freed and Peacor 1989, Niu et al. 2000, Worden et al. 2000, Aplin et al. 2006, Mondol, Jahren et al. 2008, Peltonen et al.
2009. However, many authors state it is common the reaction is complete at 100°C in many mudstones (Mondol et al., 2008, Boles and Franks, 1979, Bethke et al., 1986). The reaction is important in mudstones because it releases a range of ions that enable other minerals to precipitate, (calcite, dolomite, siderite, quartz, kaolinite, chlorite) (Worden et al., 2000b, Thyberg and Jahren, 2011, Nadeau et al., 1985, Burton et al., 1987). The smectite to illite transition also precipitates large quantities of water, as water is secreted into the pore network from smectite. Excess water often creates over-pressure in many formations, but aids hydrocarbon migration from the source rock to conventional reservoirs (Worden et al., 2000b, Leo Lynch, 1997, Freed and Peacor, 1989, Boles and Franks, 1979, Bethke et al., 1986, Aplin et al., 2006). Many authors specify K and Al ions are needed for the smectite-illite transformation reaction to take place. In some mudstones, in particular organic lean mudstones, there can be a lack of K and Al. In these particular circumstances there is little transformation of smectite-illite. (Worden et al., 2000b, Burton et al., 1987, Boles and Franks, 1979, Bethke et al., 1986).

Some authigenic clay minerals such as kaolinite can precipitate during early diagenesis, well before the depth and temperatures needed for the smectite-illite transformation reaction (Burton et al., 1987, Worden et al., 2000b, Taylor and Macquaker, 2014, Scotchman, 1989, Michalopoulos and Aller, 2004, Macquaker and Gawthorpe, 1993). Past workers have identified early clay minerals replacing detrital feldspars and/or infilling biogenic material. The latter usually occurring directly out of solution (Worden et al., 2000b, Leo Lynch, 1997, Freed and Peacor, 1989, Burton et al., 1987). Early authigenic clay mineral compositions are relatively simple (usually Si, Al, Fe and or K) with various ions readily available during early diagenesis in mudstones (Curtis, 1977, Taylor and Macquaker, 2011, Taylor and Macquaker, 2014, Macquaker et al., 2014, Macquaker and Gawthorpe, 1993, Al Balushi et al., 2013). Acidic pore water compositions associated with Si dissolution and organic matter degradation are common in shallow buried sediments are allow the precipitation of early authigenic clay minerals.

### 1.5. Concretions in mudstones

Concretions attract interest because they are so distinctive and differ compared to their host rocks. The shape, size, mineralogy and chemical compositions of carbonate can greatly vary (Coleman and Raiswell, 1995, Coleman, 1993). Concretions are observed in a range of forms, from regular spherical nodules a few centimetres in diameter with sharp defined
boundaries to laterally extensive limestone beds up to and beyond a 1m thick (Coleman, 1993).

Organic-rich mudstone/limestone cycles were first studied in the Lower Malm sections of the middle Franconian Alb, Germany, by Guenter Schuler in the 1960s (Schuler, 1967). His studies noted the visual differences seen in the Franconian formation and the sedimentological differences between organic-rich mudstones and pure limestone beds (Schuler 1967). By the late 1980’s and 1990’s organic-rich mudstone/limestone cycles were analysed in thorough detail, most notably, in the Kimmeridge Clay formation in southern and eastern England and the Blue Lias (Jet Rock), also in southern England (Coleman, 1985, Coleman and Raiswell, 1995, Bottrell and Raiswell R., 1989, Raiswell, 1988, Scotchman et al., 2000, Scotchman, 1991, Astin and Scotchman, 1988).


Raiswell 1988 studied the spherical concretions and laterally continuous limestone beds present in the Jet Rock (Blue Lias) observed in southern England. He suggested thin limestone beds present in the formation are a continuation of carbonate precipitation around the original spherical concretions. This rejuvenation of cementation is interpreted to be caused by methane reduction during later burial creating a continuous limestone horizon within the Jet Rock (Raiswell, 1988). The interpretation of methane reduction precipitating carbonate as concretions in mudstones is rare. Concretions are interpreted to be formed via other bacterial-mediated redox reactions such as; iron and in particular, sulphate reduction (Coleman and Raiswell, 1995).

Many authors (Astin, 1986, Astin and Scotchman, 1988, Berner, 1968, Coleman and Raiswell, 1995, Marshall and Pirrie, 2013, Pearson et al., 2005, Scotchman, 1991) have studied the Kimmeridge Clay Formation in the UK, which focused on concretions present
in a particular horizon between black organic-rich mudstone. Here, authors addressed the textual, mineralogical and geochemical composition of the concretions compared to the black organic-rich mudstones. All authors concluded that the concretions are diagenetic features post deposition, and formed during the early realms of burial in the sulphate reduction and decarboxylation zones (Astin and Scotchman, 1988, Macquaker et al., 1997, Scotchman et al., 2000, Scotchman, 1991).

Scotchman 1991, focused on the isotopic composition of the concretions found in a horizon between black organic rich mudstone in the Kimmeridge Clay. Primary limestones have δ¹³C ‰ values of 0 to -1‰ as they are precipitated directly from seawater. Carbonate (limestone) formed from diagenetic reactions in the subsurface has a lighter δ¹³C composition (-6 to -25 ‰) (Irwin, 1977). Sulphate reduction, iron reduction and the oxidation of organic matter all produce carbonate with a lighter isotopic signature than marine limestones (Curtis, 1977, Macquaker et al., 1997, Coleman and Raiswell, 1995, Irwin, 1977). Isotopic oxygen (δ¹⁸O‰) data indicates paleo-water temperatures at the time of deposition. Marine limestones deposited in sea water temperatures have a value of 1 to -1‰ (Irwin, 1977). Limestone formed in the subsurface are precipitated at higher temperatures due to hot pour fluids and have a more negative (lighter) value (Irwin, 1977, Coleman and Raiswell, 1995). Scotchman 1991 found the concretions in the Kimmeridge Clay were of diagenetic origin with the concretions containing isotopic signatures of -5‰ δ¹³C and -7‰ δ¹⁸O Scotchman 1991.

Carbon isotopic composition of inorganic carbon within carbonate often shows a strong connection with organic matter as a source of carbon and is one of the fundamental tools for analysing concretions (Irwin, 1977, Arthur and Anderson, 1983, Anderson and Arthur, 1983). Concretion features appear to be a location of extreme foci of bacterially-mediated processes in organic-rich sediments (Coleman and Raiswell, 1995, Coleman, 1993). These focused areas of bacteria produce the carbonate features observed in outcrop. Exopolymeric substances (EPS) that colonise small areas of the sediment-water interface are interpreted to be the cause creating microbial mats. Here, areas of intense microbial activity create a layer of “slime” like fluid that allows sulphate reducing bacteria to thrive and oxidise organic material. The product of this process is the formation of spherical carbonate concretions (Coleman, 1993, Coleman and Raiswell, 1995, Berner, 1968, Braissant et al., 2007). Spherical concretions that have formed via EPS usually contain a distinct core, which is often some form of organic material such as, wooden debris
(plant/tree debris) or biogenic material such as shell material (Braissant et al., 2007, Coleman, 1993, Coleman and Raiswell, 1995, Coleman and Raiswell, 1993).

From a petrographic perspective, first generation calcite cements precipitated as a by-product of sulphur reduction are non-ferroan, while the outer later cements blend into ferroan calcite (Scotchman, 1991). This process reflects the burial of sediments deeper into the sub-surface where they leave the realms of sulphur reduction and enter other diagenetic zones. Other elements such as manganese, sulphur and magnesium are also helpful markers of a concretions/limestone origin. Mn and Fe are usually closely related in diagenetic concretions, showing very little variation the Mn/Fe ratio. Initial cements contain high Mn content while Fe is relatively low and increases as the concretion grows. The Mn/Fe ratio decreases as cements continue to precipitate (Curtis and Spears, 1968, Curtis, 1977, Coleman, 1985, Scotchman, 1991, Astin and Scotchman, 1988). This is seen in the Kimmeridge Clay concretions, where Fe increases in the second generation calcite cements at Mn rapidly decreases due to depletion in the pore waters (Scotchman, 1991). This suggests porewaters favoured Mn sequestered into the calcites rather than Fe. This suggests the precipitation of calcite occurred below the redoxcline with conditions evolving towards a system that favours Fe precipitation within the cements (Coleman and Raiswell, 1995, Coleman, 1985, Curtis, 1977). The Mg/Fe ratio in Jet Rock and Kimmeridge Clay concretions shows an antipathetic relationship, decreasing in time as the growth of cements increases (Scotchman 1991 and Coleman 1995). The same is seen in second generation cements where the initial cement precipitated has a stable Mg/Fe content. A gradual decrease is seen in the final sparry cement around the concretion edge (Scotchman 1991).

Coleman 1995, gives an excellent summary of organic-rich mudstone/limestone cycles, whether diagenetically enhanced or, sourced from primary origins and concludes similar findings as Scotchman 1991 regarding the isotopic composition of concretions. By using basic petrographic techniques, scanning electron microscopy (SEM), isotopic and chemical analysis Coleman 1995 show how concretions are formed during early burial in varying pore water compositions. Reduced iron minerals as sulphides and low concentration ferrous iron in the sulphate reduction zone form iron poor carbonates such as calcite and dolomite. In the iron reduction zone, iron rich carbonates can still precipitate, but this is rare and low iron content minerals are more common. Such as found in the Kimmeridge Clay and Jet Rock (Scotchman et al., 2000, Scotchman, 1991, Scotchman, 1989, Macquaker and Gawthorpe, 1993, Macquaker et al., 1997, Astin and Scotchman, 1988).
2. Lithofacies of the Eagle Ford Formation
2.1 Introduction

Mudstones are the most common siliciclastic rocks in terms of volume in sedimentary basins. They are also the source and seals for petroleum systems (Taylor and Macquaker, 2014, Macquaker and Jones, 2002, Macquaker and Gawthorpe, 1993). Mudstones represent two-thirds of the sedimentary rock record holding the largest part of earth history (Schieber et al., 2000, Schieber, 1999, Bohacs, 1998). Our understanding of mudstones has significantly advanced in the last decade due to these rocks being targeted as shale gas (and oil) reservoirs (Driskell et al., 2012, Arugundade and Sohrabi, 2012, Matsutsuya, 2011, Macquaker et al., 2014). These advances have shown that mudstones mainly compose of material <62.5µm), are highly variable in composition, texture and fabrics (Taylor and Macquaker, 2011, Taylor and Macquaker, 2014, Macquaker and Adams, 2003, Macquaker, 2011, Aplin and Macquaker, 2011). These variations can be seen in every scale, from outcrop (although usually difficult), to the nanometre (Yang and Aplin, 2004, Schieber et al., 2000, Macquaker et al., 2007, Macquaker and Gawthorpe, 1993, Macquaker and Adams, 2003, Bohacs, 1998, Aplin and Macquaker, 2011). In unprepared handspecimens and in outcrop, mudstones often look homogeneous. But in well prepared core and at higher magnifications using thin sections, mudstones are highly heterogeneous (Taylor and Macquaker, 2014, Macquaker et al., 2014). Detrital sand, silt, clay, organic carbon and authigenic minerals from diagenetic processes, all influence the composition, texture and microfabric of a fine grained sedimentary rock (Macquaker et al., 2014, Taylor and Macquaker, 2014, Macquaker, 2007, Bohacs, 1998). The heterogeneity is caused by the varying quantities of the material that composes the rock- whether it is detrital clay, silt or authigenic minerals. In mudstones the composition can change at sub millimetre scales (Bohacs, 1998, Macquaker, 2014, Macquaker, 2007, Taylor and Macquaker, 2014). This reflects the changes in detrital input and/or diagenetic processes (Taylor et al., 2010, Taylor and Macquaker, 2014, Taylor, 2010, Macquaker et al., 2007, Macquaker, 2014). Mudstones can display many different fabrics and textures- such as ripples, laminations, burrows (bioturbation) and soft sediment deformation (Bohacs, 1998, Macquaker et al., 2014). These fabrics originate from many transport mechanisms that hold the fine grains in suspension and saltation. Fluid flows and flow bedload transport created by currents, waves and storms deliver the fine grained detrital components to their depositional environment, and finally the overprinting effect of burial diagenesis and compaction create the final mudstone composition (Chen et al., 2012,

The aim of this chapter is to explore 1) the lithofacies present in the Eagle Ford Fmn and identify their mineralogical, texture and biogenic content variations, 2) link the lithofacies to their interpreted depositional environment, 3) explore depositional environment variations using the identified lithofacies and core logs obtained from analysis of five Eagle Ford Fmn cores from the Bureau of Economic (BEG), Austin, Texas.

2.2 Materials and Methods

Analysis of five Eagle Ford Fmn cores was undertaken at the Bureau of Economic Geology (BEG), Austin, Texas, USA (Figure 2.0). These cores were selected based on the following criteria: (1) completeness or core interval. (2) Availability of core analysis. Each core was used to, (1) create a lithofacies scheme. (2) Determine lithofacies successions. (3) Interpret depositional environments throughout Eagle Ford Fmn deposition. The core intervals described were stratigraphically constrained to the Eagle Ford Fmn, with small portions of material from the formations overlying and underlying the Eagle Ford Fmn (Austin Chalk and Buda Limestone respectively). Not all cores were complete, with some (Shell Hay, E.D Unit #1 and Shell Leppard 1-H) only containing the Lower Eagle Ford Fmn. The Matthews J L 1-1 core contains little of Lower Eagle Ford Fmn, but has an extensive interval of the Upper Eagle Ford Fmn.

Core was described on a centimetre-scale focusing on grain type, grain size, texture, colour, sedimentary structures, diagenetic features and biogenic content. Cementation (main diagenetic feature noted in core) also influenced the facies association scheme as it is a common feature throughout the Eagle Ford Fmn. The Dunham Classification Scheme was used for identifying textural variation between the lithofacies due to the high carbonate content throughout the Eagle Ford Fmn (Dunham, 1962).
Core observations were augmented with 78 polished thin sections all cut at 20µm. These thin sections were then analysed using standard microscopic techniques to capture the microtextural and compositional properties. This was taken further again using electron microscopy (back scattered electron (BSE) imagery and energy dispersive spectrometry (SE). This was done using a Philips XL30 ESEM-FEG fitted with an EDAX Genesis EDS system. The microscope was operated at 15kV and at 10mm working distance with a resolution of 100nm.

Bulk XRD analysis was also undertaken to help identify and quantify the minerals present in each lithofacies. Qualitative and qualitative mineral composition of 44 Eagle Ford Fmn bulk rock samples was determined by a X-ray diffractometer (XRD). This analysis was undertaken at The University of Manchester and at Statoil ASA.

Rock-Eval analysis was undertaken on 22 samples to obtain TOC (%Wt). These were obtained from samples extracted from the five cores logged at the BEG, and additional data available from the BEG but were able to be correlated to a lithofacies due to the depth given. The samples extracted during the core logging were analysed at Statoil ASA, Bergen. Six core plugs were extracted from the outcrops using a rock-bore drill. These plugs were used for He-porosimetry measurements to obtain total porosities. The plugs were extracted from relatively fresh outcrop, where weathering and erosion was minimal. Analysis was undertaken at Statoil ASA, Bergen.
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<th>GPS Location</th>
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<th>Longitude</th>
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Mexico

Gulf of Mexico

Legend

- Petrology Cores
- Outcrop Study Area
- STX Edwards Reef Trend (GeoEdges)
- STX Eagle Ford & Buda Outcrop (GeoEdges)
- STX Austin Chalk Outcrop (GeoEdges)
Road out GPS location
Lat: 29.379700
Long: -101.203867

Bore holes drilled for He porosimetry measurements. Location:
Lat: 29.379714
Long: -101.203864

Bore holes drilled for He porosimetry measurements, thin section and XRD analysis. Location:
Lat: 29.379709. Long: -101.203865
2.3. Results

2.3.0 Lithofacies in the Eagle Ford Fmn

Eight lithofacies were observed through the logging and the analysis of five Eagle Ford Fmn cores, along with optical and electron-microscopy analysis on 20µm cut thin sections. The lithofacies are characterised by attributes such as; grain type, grain size, texture, colour, sedimentary structures, diagenetic features, biogenic content and TOC content. Cementation also influenced the facies association scheme as it is a common feature throughout the Eagle Ford Fmn. The following lithofacies were identified and are summarised in Table 2.3. Specific mineralogical information is displayed in Table 2.0, with Rock Eval pyrolysis in Table 2.1.

1. Argillaceous Mudstones
2. Weakly Laminated Mudstones
3. Laminated Foraminifera Rich Wackestones
4. Recrystallised Lime Wackestones (crystalline)
5. Skeletal Wackstone to Packstones
6. Bioturbated Lime Mudstone to Wackestones
7. Foraminiferal Dominated Packstone to Grainstones
8. Bentonite (Volcanic Ash)
<table>
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<th>Lithofacies</th>
<th>Core Sample, depth (ft). XRD source. (BEG, Statoil or Manchester)</th>
<th>Thin section (TS) or core correlation</th>
<th>Calcite</th>
<th>Quartz</th>
<th>Mixed layer I/S</th>
<th>Illite/ Mica</th>
<th>Kaolinite</th>
<th>Chlorite</th>
<th>Pyrite</th>
<th>Gypsum</th>
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<td>-</td>
<td>50</td>
<td>0.08</td>
</tr>
<tr>
<td>Skeletal Wackestone to Packstones (5)</td>
<td>Matthews 4673.5- Statoil</td>
<td>Core</td>
<td>2.00</td>
<td>42.20</td>
<td>0.94</td>
<td>0.05</td>
<td>426</td>
<td>580</td>
<td>7.27</td>
</tr>
<tr>
<td></td>
<td>Blumberg 4178.5 - Statoil</td>
<td>Core</td>
<td>0.08</td>
<td>0.90</td>
<td>0.32</td>
<td>0.08</td>
<td>422</td>
<td>310</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>Blumberg 4214 - Statoil</td>
<td>Core</td>
<td>0.32</td>
<td>4.82</td>
<td>0.36</td>
<td>0.06</td>
<td>425</td>
<td>473</td>
<td>1.02</td>
</tr>
<tr>
<td>Bioturbated Lime Mudstone to Wackestones (6)</td>
<td>Orts 7689.8 – BEG</td>
<td>TS</td>
<td>0.48</td>
<td>7.20</td>
<td>0.26</td>
<td>0.06</td>
<td>445</td>
<td>439</td>
<td>1.64</td>
</tr>
<tr>
<td></td>
<td>Hurt Lloyd 7139.0- BEG</td>
<td>Core</td>
<td>0.52</td>
<td>3.60</td>
<td>0.31</td>
<td>0.13</td>
<td>445</td>
<td>316</td>
<td>1.14</td>
</tr>
<tr>
<td></td>
<td>Hurt Lloyd 6737.0- BEG</td>
<td>Core</td>
<td>0.26</td>
<td>1.47</td>
<td>0.28</td>
<td>0.15</td>
<td>433</td>
<td>230</td>
<td>0.64</td>
</tr>
<tr>
<td></td>
<td>Blumberg 4223.3 – Statoil</td>
<td>Core</td>
<td>0.76</td>
<td>12.34</td>
<td>0.57</td>
<td>0.06</td>
<td>425</td>
<td>504</td>
<td>2.45</td>
</tr>
</tbody>
</table>
Recrystallised Foraminiferal dominated Packstone to Grainstone (7)  | Bretchell 3270.4 - Statoil 
| Hurt Lloyd 7294.3 - Statoil 
| Core  | Core  | Core  | Core  | Core  | Core  |
| Length (mm) | Diameter (mm) | Density (g/cc) | He-porosity (%) |
| 0.02  | 0.03  | 0.10  | 0.28  | 0.34  | 0.29  | 0.49  | 0.62  | 0.23  | 0.43  | 430  | 156  | 113  | 0.24  | 0.18  | 0.30  |

Table 2.1. Rock Eval Pyrolysis data from core samples available at the Bureau of Economic Geology and analysed at Statoil, Bergen. Other samples were measured by the BEG but could be correlated to a lithofacies from matching the depth to core logs or a known thin section sampled at that depth. There is no Rock Eval Pyrolysis for lithofacies 8.

<table>
<thead>
<tr>
<th>Lithofacies</th>
<th>Sample</th>
<th>Length (mm)</th>
<th>Diameter (mm)</th>
<th>Density (g/cc)</th>
<th>He-porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argillaceous Mudstones (1)</td>
<td>D2S3-Facies A-B</td>
<td>19.00</td>
<td>25.18</td>
<td>2.71</td>
<td>8.6</td>
</tr>
<tr>
<td>Weakly Laminated Mudstones (2)</td>
<td>Marl-facies B D253-LL-M-Facies B</td>
<td>39.55</td>
<td>31.43</td>
<td>2.50</td>
<td>2.41</td>
</tr>
<tr>
<td>Recrystallised Lime Wackestones (crystalline) (4)</td>
<td>DISI 20m East LMST DISI-ML-C-F1</td>
<td>49.76</td>
<td>41.48</td>
<td>25.18</td>
<td>25.10</td>
</tr>
<tr>
<td>Foraminiferal dominated Packstone to Grainstone (7)</td>
<td>DISI-ML-C-C1</td>
<td>40.48</td>
<td>25.19</td>
<td>2.70</td>
<td>2.6</td>
</tr>
</tbody>
</table>

Table 2.2. Helium porosimetry measurements of six mini cores that were bored out of the Eagle Ford Fmn outcrops in southwest Texas (coordinates 29.3797, -101.2038, see Figure 2.0). Porosity measurements are only available for lithofacies 1, 2, 4 and 7.
<table>
<thead>
<tr>
<th>Lithofacies</th>
<th>Main minerology (XRD) % (average)</th>
<th>Colour</th>
<th>Main Grains Present</th>
<th>Sedimentological Characteristics</th>
<th>TOC (wt%)</th>
<th>Φ %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calcite</td>
<td>Quartz</td>
<td>Clays</td>
<td></td>
<td></td>
<td>Avg %</td>
</tr>
<tr>
<td>1 Argillaceous Mudstone</td>
<td>29 (n=6)</td>
<td>22 (n=6)</td>
<td>44 (n=6)</td>
<td>Black to very dark green/brown</td>
<td>Mixed layer f/S. Kaolinite/chlorite, planktonic (globigerinid) foraminifera</td>
<td>~5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Faintly laminated- sometimes massive. Ripple laminae are common. Some burrowing is present but extremely rare.</td>
<td>(n=3)</td>
</tr>
<tr>
<td>2 Weakly laminated Mudstone</td>
<td>47 (31-55)</td>
<td>18 (10-24)</td>
<td>27 (20-40)</td>
<td>Black</td>
<td>Mixed layer f/S. Koalinite/chlorite, planktonic (globigerinid) foraminifera. Inoceramid bivalves</td>
<td>~6.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Thin (sub mm) planar but truncated laminae. Some are wavy but are only present at the bottom of packages where they transition from the Argillaceous Mudstones Contain sharp or erosive contacts.</td>
<td>(n=3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Planar laminated. Laminations consist of foraminifers. Some laminae resemble ripples, although this is rare. Burrowing is present.</td>
<td>(n=4)</td>
</tr>
<tr>
<td>4 Recrystallised Lime Wackestones (crystalline)</td>
<td>90 (79-94)</td>
<td>5 (2-10)</td>
<td>5 (3.5-7)</td>
<td>Light Grey</td>
<td>Recrystallised carbonate cements cements</td>
<td>Highly cemented with calcium carbonate. Crystalline texture. Cement grains in size from 20-100µm. Fractures are infilled and closed with carbonate, though rare.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Strongly laminated and bedded. Cross laminations and imbricated bedding. Scoor and truncated laminae surfaces. Skeletal fragments most dense at base of units and become more rare- fining up.</td>
<td>(n=2)</td>
</tr>
<tr>
<td>5 Skeletal Wackestone to Packstones</td>
<td>73 (65-86)</td>
<td>8 (4-14)</td>
<td>12 (5-18)</td>
<td>Medium to light grey</td>
<td>Fragmented Inoceramid bivalves, Globigerinid Foraminifera, Peloids, phosphate grains. Fish bones and teeth.</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Strongly laminated and bedded. Cross laminations and imbricated bedding. Scoor and truncated laminae surfaces. Skeletal fragments most dense at base of units and become more rare- fining up.</td>
<td>(n=3)</td>
</tr>
<tr>
<td>6 Bioturbated Lime mudstone to Wackestone</td>
<td>84 (76-88)</td>
<td>7 (2-14)</td>
<td>8 (3-11)</td>
<td>Dark grey to light grey</td>
<td>Bivalves, foraminifera, radiolarians and unidentifiable skeletal material.</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Bioturbated. Moderately recrystallised with calcium carbonate. Fractures are infilled and closed with carbonate, though rare. Skeletal fragments are calcified, some are phosphotosed, though rare.</td>
<td>(n=4)</td>
</tr>
<tr>
<td>7 Foraminiferal dominated Packstone to Grainstone</td>
<td>89 (85-98)</td>
<td>4 (1-9.7)</td>
<td>4 (0-7)</td>
<td>Light Grey</td>
<td>Carbonate cements. Benthic foraminifera, unidentifiable skeletal material</td>
<td>Recrystallised. Fractures are infilled with calcium carbonate. Commonly interbedded with skeletal wackestones and packstones.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Commonly massive, although some beds do contain planar laminae. Heavily bioturbated.</td>
<td></td>
</tr>
<tr>
<td>8 Bentonite (Volcanic Ash)</td>
<td>10 (n=1)</td>
<td>5 (n=1)</td>
<td>72 (n=1)</td>
<td>Green-grey-yellow</td>
<td>Bioclasts, large skeletal fragments and teeth.</td>
<td>Commonly massive, although some beds do contain planar laminae. Heavily bioturbated.</td>
</tr>
</tbody>
</table>

Table 2.3. Summary of the Eagle Ford Fmn lithologies showing mineralogical composition, colour, sedimentological characteristics and total organic carbon (TOC).
2.3.1 Argillaceous Mudstone

The argillaceous mudstones are black to dark brown in colour; however some (although rare) are greenish/brown-black in colour (Figure 2.1). The argillaceous mudstones are an organic and clay-rich lithofacies. Total organic carbon (TOC wt %) values for this lithofacies range from 4-6 wt%, with the average of 5 wt%.

The argillaceous mudstones are only found in the lower section of the Eagle Ford. The bulk of the facies is found directly above the Buda limestone-Eagle Ford contact, but commonly appears again further up the stratigraphy in small (<1m) packages (see figure 2.9). The contact between the Buda Limestone and the Eagle Ford is sharp and erosive. In two cores observed, the argillaceous mudstones are the lithofacies present at the contact. In cores in the south or west, the argillaceous mudstone are missing (Figure 2.1).

The argillaceous mudstones vary in thickness, with some units only 0.04m thick and others >2m, although such large units are rare. A key characteristic is defined by their fissility in core. When handling fresh samples in hand specimen they often break apart along very faint laminae, which are not visible until they break apart- highlighting their fissility. The argillaceous mudstones are predominantly massive containing floating silt-sized grains. With a hand lens and in thin section foraminifera have accumulated along laminae to produce sub millimetre, but distinct thin laminations. However, foraminifera are rare. In thin facies, floating silt-sized particles are mainly dolomitic rhombs (figure 2.0). Phosphate grains are common in core and are often 1-2mm in diameter. They are mainly found at the base of contacts with the Buda-limestone or other underlying lithofacies.

In thin section the silt-sized fraction (>62.5µm) contain planktonic Hedbergella foraminifera (Globigerina). Their chambers are infilled by calcite, and/or kaolinite (figure 2.0). Fragments of inoceramid biovalves are present but are unevenly distributed throughout the facies, unlike the foraminifera, which are evenly spread throughout. Some areas of the facies are sparse of inoceramid biovalves while certain zones contain many fragments (Figure 2.1). All inoceramid fragments lie parallel to bedding. Sedimentary structures such as ripples and sub millimetre traction laminae consisting of organic rich mud drapes are present. Pyrite framboids are present in this facies but are low in quantity compared to other lithofacies. Electron microscopy indicates silt-sized detrital quartz grains are present within the matrix, but the majority of quartz is observed as much finer (5-10µm) cements (Figure 2.1).
Six samples were used to undertake XRD analysis (see Table 2.1). The argillaceous mudstones are the most clay rich lithofacies (average ~44%) in the Eagle Ford Fmn. Mixed layer illite/smectite (I/S) are the main clay constituents (~21%) along with smaller quantities of illite (16%) and authigenic kaolinite (~5%) and chlorite (~2.5%). Calcite comprises on average, ~29% of the assemblage, while quartz comprises ~22%. Plagioclase and K-feldspar on average comprise ~0.4% and ~1.6% respectively.

In core and transmitted light under thin section this facies has no visible porosity. Only under electron microscopy can porosity be identified. In the argillaceous mudstones, the majority of porosity is found as micro-porosity between clay minerals and within organic matter. Whether this porosity produces any significant permeability is still unknown (Pommer et al., 2014, Fishman et al., 2013b).

Rip up clasts are common, as are large pebble sized phosphate grains and fish bones/teeth. Ripples and hummocky cross stratification are common in the lower 5m of the Eagle Ford Fmn. In thin section sub millimetre traction laminae consisting of organic rich mud drapes are present.

The argillaceous mudstones transition into the weakly laminated Mudstones (lithofacies 2). The boundary between the two is difficult to determine, however XRD shows a gradual decrease in clay and quartz content, while calcite content increases. Under transmitted light foraminifera are a lot more common, while mud drapes and ripples become rare, suggesting a transition to more pelagic, calmer environments.

*Interpretation of the Argillaceous Mudstones*

The presence of sub-millimetre clay lenticular traction laminae consisting of organic-rich mud drapes suggests bottom water currents were present transporting and re-distributing clastic material at the seabed. Ripples and mud drapes are also an indication of being deposited just below storm-wave base.

The transition from clean water carbonates (Buda Limestone) to organic rich muds (Eagle Ford) is interpreted to be a sequence boundary. There is no evidence for aerial exposure of the carbonate platform through sea level fall, but the argillaceous mudstones are interpreted to be a regressive systems tract that overlies the highstand. These types of sequence boundaries are associated with erosional surfaces and significant marine hiatuses (Schlager, 2005).
Core comparisons show that the argillaceous mudstones are not uniform across the entire Eagle Ford Fmn area (figure 2.9). Thin sections sampled from cores in the southwest of the formation display less ripples and traction laminae. They display settling through suspension suggesting a more pelagic environment. Foraminifera content increases and clay content decreases. Samples from the northeast display more clastic material, likely to be sourced from the East Texas Woodbine Delta, along with other shelf structures. Here the facies is comparably thick and overall thins towards the southwest. With the combined observations of decreasing terrestrial material, the lack of sedimentary structures and increasing foraminifers in the southwest, it is thought the southwest of the Eagle Ford Fmn is distal and likely to be in a more open marine environment.
Figure 2.1. Argillaceous Mudstone. Outcrop, core, thins section in plain light microscopy and electrical microscopy photomicrographs. A. Outcrop photograph at Osman Canyon, West Texas, and displaying argillaceous mudstone at the bottom of the Eagle Ford. Note, cross beddings and ripples (red arrows), pen for scale. B. Core photograph from the J A Leppard 1-H core, (depth 13,555 ft), showing black/greenish, fissile argillaceous mudstones displaying weak laminations, ripples and cross stratification (green arrow). In places the argillaceous mudstones are massive and contain few floating silt sized grain (red arrow). C. Thin section micrograph from Leppard 13,555.4 (see core log), illustrating the lack of foraminifera in the
argillaceous mudstones and high clay content. A heterohelix planktonic foram is (red arrow), present in the centre infilled with kaolinite. The other white flecks are silt sized dolomite rhombs (green arrow). D. Thin section micrograph sampled from the Hay core (13,825.7) illustrating sub-millimetre scale ripples, organic-rich mud drapes (green arrows), ripples and planktonic foraminifera infilled with calcite cement and kaolinite (red arrow). E. Scanning Electron Microscope (SEM), photomicrograph of the same sample in C. The matrix is comprises of coccolith fragments (green arrow), illite and mixed layer illite/smectite with calcite and kaolinite infilled foraminifera in the centre, (red arrow).

2.3.2 Weakly Laminated Mudstones

The weakly laminated mudstones are similar in appearance to the argillaceous mudstones in core. They are mainly black in colour with some sections, especially in cores from the northeast of the formation, having a brownish-black colour (figure 2.2). This facies is the most organic-rich with TOC values averaging 6.2 wt%

The weakly laminated mudstones have the biggest range in thickness with some units only 0.02m and others >5m. This facies is more cemented unlike the argillaceous mudstones that have a fissile characteristic. Planktonic Hedbergella foraminifera (Globigerina) are common and are the main silt sized (>62.5µm) component found in this facies along with fragmented inoceramids. Both are found mainly in sub millimetre to millimetre scale planar laminae (figure 2.1). Some laminae are truncated or contain wavy ripples, although the latter are rare and are only visible through optical microscopy. Poly-framboidal pyrite and phosphatic fragments are less common but are always present in thin section (figure 2.1).

XRD analysis (8 samples) shows a key compositional difference between the laminated foraminiferal mudstones and the argillaceous mudstones is calcite content. This facies contains mainly calcite (average 47%). Clay minerals constitute on average 27%, quartz 18% and plagioclase and K-feldspar (3.1% and 1.8% respectively). Clay mineral XRD shows clay mineral composition is mixed layer I/S (average 12%), illite (average 9%) kaolinite (average 4.5%), chlorite (average~1.1%).

Thin section analysis through plane polarised light shows the accumulation of planktonic foraminifera’s along traction laminae. The foraminifera’s are well sorted with the majority infilled with calcite cement (some foram chambers are infilled with kaolinite) (figure 2.1). There is no visible porosity in core or thin section under plane polarised light. Under
electron microscopy clay held micro-porosity is visible. Intra-crystalline porosity is present within cement grains that infill incoceramid bivalves and planktonic foraminifera’s. The bulk of porosity however is found within the organic matter when it has matured and expelled hydrocarbons. Total porosity for these samples is 9.3% (table 2.1).

The boundary from the weakly laminated mudstones to the laminated foraminiferal rich wackestones is difficult to identify visually. However, the transition between the two is distinguishable due to foraminifer and calcite content increasing, with clay mineral content decreasing.

Figure 2.2. Laminated Mudstone in outcrop, core, thin section in plain polarised light and electrical microscopy. A. Outcrop photograph of a road cut in west Texas displaying the weathered Laminated Mudstone (green arrows) containing concretions and thin limestone beds (red arrows). B. Core photograph of J A Leppard 1-H core at depth 13,566.2 showing the characteristic black, faintly laminated (red arrow) mudstones. C. Thin section sampled from the J A Leppard 1-H core (13,566.2- see core log 2.1) illustrating sub-millimetre scale planar laminae (green arrow). Some laminae are truncated or contain wavy ripples,
although the latter are rare. Organic rich mud drapes are also rare, unlike in the argillaceous mudstones. Organic matter is more evenly spread throughout the matrix and not concentrated within mud drapes. Small planktonic foraminifera (<180µm) is infilled with calcite cement and kaolinite (red arrow). D, Scanning Electron Microscopy (SEM), photomicrograph of the same sample in C, showing the matrix is mainly coccolith fragments (blue arrow), (more abundant than the argillaceous mudstone), illite and mixed layer illite/smectite with calcite (red arrow), and kaolinite (green arrow), infilled foraminifera chambers.

**Interpretation of the Weakly Laminated Mudstones**

The lack of distinct sedimentary structures such as lenticular laminae present in core and thin section, suggest the laminated foraminiferal mudstones were deposited in deeper, lower energy environments, below storm wave base compared the argillaceous mudstones (Donovan et al., 2012, Liro et al., 1994). Due to the high organic carbon content, the lack of benthic species, inoceramid bivalve content, the facies was likely to be deposited in suboxic to anoxic conditions (Pederson and Calvert, 1990, Tyson, 2005, Wignall, 1994, Kauffman, 1984). The presence of planar laminations can suggest sediment was deposited through pelagic and hemipelagic fallout, where sediments in suspension settle onto the seabed (Wignall, 1994, Arthur and Sageman, 2004, Donovan et al., 2012, Longman et al., 1998). However more recently, workers (Schieber et al., 2010, Schieber, 1999, Taylor and Macquaker, 2014, Taylor, 2010), have shown how fine-grained sediments can be re-worked at the sediment water-interface. Slope driven turbidities and/or bottom water currents create ripples and truncated laminae. When these are compacted during burial they can create planar laminae in core and thin section (Schieber et al., 2010, Schieber, 1999). Intermittent low energy currents reworking fine-grained sediment were probably present during storm events creating distinct laminae observed in core (Longman et al., 1998, Donovan et al., 2012, Kauffman, 1984). Storm events were likely to occur in the Western Interior Seaway with low pressure systems sweeping in from the Gulf of Mexico just like present day Hurricane systems (Donovan et al., 2012).

**2.3.3 Laminated Foraminifera-rich Wackstones**

The laminated foraminiferal-rich wackstones are mainly grey to dark-grey in colour, but sometimes black (Figure 2.3). Millimetre-scale (>1.5mm) planar and traction laminae, give a pin-stripe like appearance in some instances. Bioturbation is still low in this facies, however in places the lithofacies is lightly mottled. The laminated foraminiferal-rich
wackstones are the biggest lithofacies by volume within the Eagle Ford Fmn (figure 2.9). The facies is particularly common in the upper sections of the Lower Eagle Ford Fmn and lower section of the Upper Eagle Ford Fmn (figure 2.9). Sections of this facies vary from 0.5cm to >2.2m. The transition from weakly laminated mudstones into the laminated foraminiferal rich wackstones is quite distinct where the quantity of foraminifera increases and colour is lighter (Figure 2.3).

The laminated foraminiferal-rich wackestones contain benthic and planktonic foraminifera. Planktonic species have decreased in content with benthic foraminifera the more dominant type observed in thin section (Figure 2.3). Like other lithofacies foraminifera are the dominant silt sized (>62.5µm) component, but in this lithofacies they are a key component, being considerable bulk of overall rock volume. Benthic forams are entirely of the *Neobulimina albertensis* and *Neobulimina canadenis* species (Figure 2.3). Foraminifera are well sorted (~50µm in diameter), and accumulate along planar laminae creating millimetre-scale laminations. Few isolated foraminifera are present in the micritic matrix (0.06µm-62.5µm). Skeletal debris are common, particularly within the darker grey, organic clay-rich segments. Thin section analysis reveals inoceramid bivalve fragments are the dominant debris component, which range in size (0.5mm-2.5mm). They lie in situ to bedding (figure 2.3). Poly-frambodial pyrite is common and fragments of fish bones converted to large phosphatic grains. XRD analysis (7 samples), indicates this facies predominantly comprises calcite (average ~62%), clay content is ~14%, quartz ~15% and plagioclase and K-Feldspar both ~2%. The clay mineral fraction is mainly mixed layer I/S (~6%) with illite ~5% and kaolinite 3.2%. TOC values decrease to 3.8 wt% with some samples containing 5 wt% total organic carbon. The bulk of calcite is observed as coccolith fragments within the micritic matrix and within the foraminifera chambers where they have been infilled with calcite cement (Figure 2.3). Some test walls have recrystallised and have allowed for foraminifera chambers to join together. Additional authigenic calcite cement can often surround the tests. The infilling of foraminifera chambers is likely to have occurred during early burial due to the preservation of most foraminifera tests. Some foraminifera do possess minor damage such as, gentle miss-shaping and micritisation of their chamber walls (Figure 2.3). Micro fractures present in core are the only features that display porosity in the laminated foraminiferal rich wackstones, although most fractures are mineralised with calcite cement.
(Figure 2.3). Electron microscopy shows a change in porosity characterisation in this facies. A significant quantity of porosity is intra-particle porosity where pores are present within authigenic calcite grains. The pores present here are much larger (~3µm) compared to the pores found in organic matter (~0.2µm). Organic porosity is present but constitutes less of the total porosity in the laminated foraminiferal rich wackstones due to less TOC content.

Interpretation of the Laminated Foraminiferal - rich Wackestones

The laminated foraminiferal-rich wackestones are typically found interstratified with the laminated foraminiferal mudstones in the Lower Eagle Ford Fmn (Figure 2.1and Figure 2.9). They are also present in the middle and lower sections of the Upper Eagle Ford Fmn (figure 2.9). This facies is interpreted as late-transgressive - to early highstand deposits (Bohacs, 1998, van Buchem et al., 2005, Stefani and Burchell, 1990, Creaney and Passey, 1993). The main mechanism of deposition for the laminated foraminiferal rich wackestones is through pelagic and hemipelagic fallout (Donovan et al., 2012).

Concentrations of skeletal material and foraminifera’s create distinct laminations and defined erosive bases which suggest reworking by bottom water currents (figure 2.3). These are interpreted to be reworked syn-deposition just within storm wave base (Tucker and Wright, 1990). The darker segments of the facies suggest an oxygen deficient environment at the sediment-water interface due to the dominant presence of inoceramid bivalves (Kauffman, 1984, Longman et al., 1998, Lowery et al., 2014). The presence of benthic foraminifera suggests an increase in oxygen and nutrient content within the water column and surface waters (Lowery et al., 2014, Donovan et al., 2012, Corbett and Watkins, 2013). Although planktonic foraminifera are still present, the presence of significant benthic foraminifera suggest an end of ideal conditions for source rock deposition and the transition to oxygenated, overturning marine environments with a possible rise in overall sea-level (transgression) (Lowery et al., 2014, Corbett and Watkins, 2013, Kauffman and Sageman, 1990, Kauffman, 1984).
Figure 2.3. Laminated foraminiferal-rich wackestone in outcrop, core, thin section in plain polarised light and electrical microscopy. A. Outcrop photograph of a road cut in west Texas (GPS coordinates: Lat 29.3797, Long -101.2038) displaying the weathered Laminated foraminiferal-rich wackestones. Green arrow denotes beds of higher carbonate content with the red arrow highlighting areas of lower content. Bed thickness is often < 5 cm. B. Core photograph (Matthews core, depth 4671.3) showing the characteristic grey to dark grey, pin stripe appearance (red arrow). Green arrow displays larger beds present in the lithofacies. C. Thin sections scan sampled from the Lloyd Hurt core (7262.5 & 7233.80 respectively), illustrating
millimetre scale planar laminae (red arrow). The majority of the grey-white material is infilled benthic foraminifera. D. Thin section micrograph of the Hurt Lloyd thin section (7262.5) in C. Benthic foraminifera (Neobulimina albertensis and Neobulimina canadenis) are common within the assemblage (green arrow) and are infilled with calcite. Foraminifers infilled with kaolinite are rare. Other species of fauna present in this lithofacies, probably due to increased oxygen content. The red arrow denotes a calcisphere. E. Scanning Electron Microscopy (SEM), photomicrograph of the same sample in C, showing the matrix is mainly coccolith fragments (blue arrow), illite and mixed layer illite/smectite with calcite (red arrow) infilling foraminifera chambers, and pyrite (green arrow). F. Core photograph (J-W Blumburg, depth 4298.0 ft) of a mineralised fracture in the laminated foraminifer-rich wackestones.

2.3.4 Recrystallised Lime Wackestones

The recrystallised lime wackestones are a common lithofacies present in the lower Eagle Ford Fmn (Figure 2.4), found as definitive, continuous carbonate beds, and as “football” shaped concretions (Figure 2.4) within the organic-rich weakly laminated mudstones in outcrop (Figure 2.4). They appear along specific stratigraphic horizons and are small in terms of total rock volume in the Lower Eagle Ford Fmn (Figure 2.9). The recrystallised lime wackestones are light grey in colour in both outcrop and core (figure 2.4). Their colour is due to high quantities of carbonate cement and low quantities of clay minerals (Figure 2.4). There is no organic matter observed in this facies (Table 2.1).

In outcrop and core, the recrystallised lime wackestones appear massive and homogenised, with no visual indications of bioturbation or hydrodynamic sediment sorting at the sediment water interface. In thin section they are crystalline, with little of the the original deposition texture present (Figure 2.4). Foraminifera are often fragmented and recrystallised, although some remain preserved (Figure 2.4). Some beds contain calcified radiolarians and are only identifiable due to recrystallisation and calcification. Planktonic planktonic foraminifera are observed with no benthic species observed, however it is impossible to tell if other biogenic species were present due to recrystallisation and heavy cementation. The recrystallised lime wackestones are mainly comprised of angular, diagenetic calcite cement grains (Figure 2.4). The size of cement grains varies (10µm - 100µm) between the concretion types (see chapter 4). In the football concretions the cement grains are typically much smaller (10 - 40µm) compared to the continuous concretional beds that are present in outcrop (40-100µm). Cathodoluminescence highlights the variations of brightness between individual cement grains and variations (zonations)
within a single cement grain (Figure 2.4). The carbonate cements display a bright, non-ferroan luminescence, while the calcareous matrix between the cement grains displays a dull, non-ferroan luminescence.

XRD analyses shows that on average 90% of the mineralogy is calcite (range 79-94%), with small (5%) quantities of clay minerals (mixed layer I/S – 0.7%, kaolinite 4.2%) and a small quantity of quartz, 5%. K-feldspar and plagioclase are not present in this lithofacies.

Interpretation of the Recrystallised Lime Wackestones

The recrystallised lime wackestones are observed at top of successions containing the previous lithofaies (1, 2 and 3). The recrystallised lime wackestones are interpreted to represent deposition during sea-level highstands (Bohacs, 1998, Bohacs, 1990). The lack of organic matter and the subsequent colour of lithofacies, and the presence of benthic foraminifera suggest a more oxygenated environment relative to the previous facies mainly found in the Lower Eagle Ford Fmn (Pederson and Calvert, 1990, Tyson, 2005, Wignall, 1994). This lithofacies is discussed in much greater detail in chapter 4, exploring the distribution, types and distribution of the lithofacies in the Lower Eagle Ford Fmn.
Figure 2.4. Recrystallised lime wackestone in outcrop (football concretion and limestone bed), core, thin section and cathodoluminescence. A. Outcrop photograph (GPS coordinates: Lat 29.3797, Long -1012029) of a road cut in west Texas displaying a football concretion (red arrow - recrystallised lime wackestone) within organic rich, laminated mudstone in the lower Eagle Ford Fmn (note scale bar on right). B. Core photograph (section slabbed from Statoil/Talisman core at unknown depths) displaying the edge of a football concretion (yellow arrow) and a limestone unit below it (blue arrow). C. Thin section micrograph (thin section D2) displaying the micritic (fine calcite crystals) that dominate the recrystallised lime wackestones.
Calcified radiolarians are common (red arrow), as are pyrite framboids (yellow arrow) and clay rich nodules (blue arrow) that are interpreted to be originally pellets. **D.** Core photograph (J H Leppard 1-H 13590.93) displaying the edge of a football concretion (yellow arrow). **E.** Thin section micrograph of a recrystallised lime wackestone (thin section C1) with larger cement grains compared to C, thus indicating a slower precipitation of carbonate cements to create larger crystals (yellow arrow). **F.** Identical image to E, but in cathodoluminescence. Blue arrow denotes bright luminescing calcite cement compared to the duller cements grains surrounding it. The yellow arrow denotes zonation’s in cement crystals. Both highlight changes in pore water chemistry as carbonate is precipitated. Most likely a depletion in iron as it is sequestered into pyrite during early burial.

### 2.3.5 Skeletal Wackestone to Packstone

This lithofacies is distinctive due to its bedding and colour giving a thick pin-stripe appearance. The skeletal wackestones to packstones are characterised by millimetre to centimetre scale cross laminated beds which, are eroded at the base (Figure 2.5). These laminated beds often vary in colour (dark grey to grey, to light grey), giving the faces its thick pin striped appearance (Figure 2.5). The colour of the beds is dependent on the level of carbonate cementation and the biota content within them. Lighter coloured beds consist of whole and fragmented inoceramid debris that are found at random and at bedding orientation. Recrystallised carbonate cement grains are common in the lighter grey beds. Unidentifiable skeletal fragments are present throughout the facies and are randomly oriented to bedding (Figure 2.5). In plane polarised light under thin section the darker beds of the skeletal wackstone to packstones are characterised by a clay to silt-size matrix (0.06 to 62.5µm) that contain abundant organic matter (2-3 TOC%), inoceramid fragments and floating foraminifera’s (Figure 2.5). Planktonic foraminifera (*Heterohelix, Hedbergella*), benthic foraminifera (*Neobulimina*), and inoceramid bivalves are the dominant biota present in the skeletal wackstone to packstones. They are accompanied with pyrite framboids, phosphate grains, peloids and other curved skeletal fragments, likely to be coccolith debris (Figure 2.5).

Electronic microscopy shows the skeletal wackstone to packstones have a similar clay/micrite matrix to the laminated foraminifera rich wackstones (lithofacies 3). The majority of clay in this facies is authigenic mixed layer I/S, with small quantities of kaolinite, usually inside foraminifera chambers (Figure 2.5). The majority of calcite
cement is within foraminifera chambers and inoceramid bivalves. Quartz cements are common and are seen attached or on top of calcite cements.

XRD analysis shows this facies is rich in calcite (~73%). Clay content is ~12% with mixed layer I/S and illite the main constituents of the clay fractions (4.6 and 4.5% respectively). Kaolinite constitutes the rest of clay fraction ~2.3%. Electron microscopy shows the majority of kaolinite is within the foraminifera’s with some grains present in the micrite matrix. Quartz is ~7% of the composition with plagioclase and K-feldspar ~1.2% and ~0.7% respectively. TOC values in the skeletal wackstone to packstones vary. Average TOC wt% is 2.4 wt%. The higher TOC contents (up to 3.5 wt%) are found in the darker sections of the lithofacies with the lower TOC values (0.5-1 wt%) in the lighter cemented sections.

**Interpretation of the Skeletal Wackestones to Packstones**

The skeletal wackstone to packstones are a common lithofacies in the Middle and Upper Eagle Ford Fmn where they intermit with the laminated foraminiferal-rich wackestones (lithofacies 3), bioturbated lime mudstones (lithofacies 6) and foraminiferal dominated packstones to grainstones (lithofacies 8) (Figure 2.9). The skeletal wackstone to packstones are also present at the top of the Lower Eagle Ford Fmn as centimetre thick beds within the argillaceous mudstones (lithofacies 1) and weakly laminated mudstones (lithofacies 2).

Due to the pin stripe appearance, erosive bases, centimetre scale sedimentary structures and fauna assemblage; the skeletal wackstone to packstones are interpreted to be mid-transgressive to highstand deposits that were deposited in sedimentation events into a background of mudstone (Flugel, 2010, Bohacs, 1998). The lighter grey intervals commonly display erosive bases, cross-ripple laminations and sharp basal contacts, which are all indicators of turbidite deposits during periods of relatively high sea level (Flugel, 2010, Cook and Mullins, 1983, Tucker and Wright, 1990). Periods of lower sedimentation rates are interpreted to define the darker grey beds, which represent oxygen deficient, suspension deposition environments creating organic-rich segments.
Figure 2.5. Skeletal Wackestone to Packstone in core and thin section. A. Core photograph (J-W Blumberg 4136.35 ft) displaying the pin stripe appearance of the skeletal wackestones to packstones, which represent thin, cyclic stacked units (yellow arrow) with sharp and sometimes eroded contacts (red arrow). Ripples cross-laminations (blue arrow) and planar laminations (dotted red line) are common and are thought to represent bottom water currents and disturbance, suggesting this interval of the lithofacies was a turbidite deposit. Green arrow denotes a large (0.5cm) phosphatic fragment, likely to be a piece of organic material originally. B. Core photograph (J-W Blumberg 4136.86 ft) displaying randomly orientated skeletal material
(red arrow), within ripple cross laminations (green arrow) and eroded contacts (red dotted line). C. Thin section scan (Orts 7694.0) showing skeletal material lying in parallel to bedding. Inoceramid bivalves (red arrow) and skeletal material (green & yellow arrows) are common. D. Thin section micrograph (Orts 7694.0) displaying small skeletal fragments (yellow arrow) and a large bone fragment that traverses the thin section (red arrow). E. Thin section micrograph (Wagner Bros 6240.50) of a faunal rich skeletal packstone full of benthic foraminifera (green arrow) and phosphatised bone fragments (red & yellow arrows). F. Identical thin section micrograph in CL. Bright fluorescing, non-ferroan calcite infills foraminifera chambers (red arrow). Foraminifera walls remain non fluorescing (green arrow). Skeletal fragments fluoresce but are generally dull compared to the forams (yellow arrow). Some skeletal material is completely phosphatised and does not fluoresce. Blue fluorescing forams indicate kaolinite is present within them.

2.3.6 Bioturbated Lime Mudstone to Wackestone

The bioturbated lime mudstones to wackestones are distinctive and easy to identify in core due to their light-grey to grey colour (Figure 2.6). Extensive bioturbation and moderate cementation produce a homogenised looking rock that varies little in colour and composition in core (Figure 2.6). No sedimentary structures are present except for erosive contacts at the top of some units and burrows. Burrows are defined by thin, slightly darker grey lines in core. Foraminifera are difficult to spot due to the lithofacies colour, but with a hand lens the larger specimens can be seen floating among the calcareous matrix (Figure 2.6). The bioturbated lime mudstones to wackestones are mainly found in the Upper Eagle Ford Fmn and Middle Eagle Ford Fmn (Figure 2.9). Unit thickness is commonly between 5-30cm with beds rarely smaller or larger.

In core, unidentified larger skeletal debris are visible, while in thin section smaller fragments are more common (Figure 2.6). Thin section analysis reveals the bioturbated lime wackstones are rich in benthic foraminifera, with some planktonic forams present, though rare. Bivalve and echinoid fragments along with calcispheres, ostracods and calcified radiolarians are also common. All biota have been preserved to a degree by the infilling and/or replacement of calcite (figure 2.6). CL indicates that the calcite is non-ferroan and a high quantity of the calcite is precipitated in one phase (figure 2.6). Electron microscopy highlights the micritic matrix (3-7µm) and the larger calcite cements within and surrounding the fauna (figure 2.6). Clay and organic matter content is small and is seen in small quantities within the micritic matrix. Organic matter is sporadic and occurs as small flakes (~5-6µm) (figure 2.6).
XRD analysis shows the bioturbated lime wackstones are a carbonate rich lithofacies. Calcite values are on average ~84%, clay minerals ~8%, quartz ~7%, plagioclase ~1% and K-feldspar 0.2%. TOC values for this facies are low compared to the former facies, with average values less than 1% (Table 2.1).

In core and thin section in plane polarised light there is no visible porosity. Electrical microscopy shows that the bioturbated lime mudstones to wackstones contain significant intra-particle porosity. This is mainly found within the biota and the cements that infill and surrounds them. There is little organic porosity found within these samples due to the low organic content. Compared to the previous lithologies, the bioturbated lime wackstones have a different porosity network where a vast majority of the pores are larger than 1µm.

*Interpretation of the Lime Mudstone to Wackestones*

The bioturbated lime mudstones to wackstones are seen near, or at the top of parasequences relative to the previous lithofacies (4 and 5), (4 and 5) in the Middle and Upper Eagle Ford Fmn suggesting they are highstand deposits (Figure 2.9). Benthic organisms, large bone fragments, extensive bioturbation and low organic carbon content suggest the bioturbated lime mudstones wackstones were deposited during sea-level highstands in shallower and oxygenated environments (Flugel, 2010, Mulder and Alexander, 2001, Cook and Mullins, 1983, Friedman, 1964). We interpret this lithofacies to be the Middle and Upper Eagle Ford Fmn equivalent of the recrystallised lime wackestones (lithofacies 4) in the Lower Eagle Ford Fmn, due to their similar distribution in outcrop and core, their composition, but with the addition of bioturbation and richer abundance of faunal species due to oxygen content (Al Balushi et al., 2013, Flugel, 2010, Friedman, 1964).
Figure 2.6. Bioturbated lime mudstones to wackestone. A. Core photograph (Matthews J L 11, depth 4598.63 ft) displaying the homogenous appearance of the bioturbated lime mudstones to wackestones. Green
arrow denotes a burrow, which is darker in colour. Erosive contacts are common (red arrow). **B.** Thin section micrograph (Hurt Lloyd 7298.75) displaying calcite infilled benthic foraminifera (red arrow & BF). Green arrow denotes burrows within the calcareous matrix. Calcispheres (C) are common in the bioturbated lime mudstones to wackestones. **C.** Thin section micrograph (Hurt Lloyd 7298.75) under CL showing equal fluorescing calcite cements. Foraminifera (F) are sometimes infilled with kaolinite, fluorescing a dark blue colour. The outline of an ostrapod (O) is visible under CL due to the duller luminescing shell wall. Calcispheres (C) are common and are distinct due to a non-luminescing shell wall. **D.** Core photograph (Matthews J L 11, depth 4591.14ft) displaying biturbation (B) and skeletal fragments (SF). **E.** Thin section scan of a bioturbated lime mudstone to wackestone Note, the homogeneous appearance and light grey colour indicating little organic matter or clay content. **F.** SEM micrograph of Hurt Lloyd 7298.75. Calcite cements dominate the bioturbated lime mudstones to wackestones with little clay minerals or organic matter. Foraminifera (F) and calcispheres (C) are common and are infilled by authigenic calcite cements. Pyrite (P) infills some foraminifera and calcispheres, but is rare.

### 2.3.7 Foraminiferal dominated Packstone to Grainstone

The foraminiferal dominated packstone to grainstones are typically light grey to white in appearance in core and outcrop (Figure 2.7). They are mainly found at the top of the Upper Eagle Ford Fmn and present at the Eagle Ford Fmn - Austin Chalk contact/transition (Figure 2.9). The lithofacies is also present in the Middle Eagle Ford as very thin 0.2-1cm thick intervals occurring immediately above the skeletal wackestones to packstones or bioturbated lime mudstones to wackestones. Intervals are present in all cores analysed and hint at a cyclic trend of deposition.

The foraminiferal dominated packstone to grainstones mainly display well defined top and bottom contacts, although it is common for both to be gradational in some intervals (Figure 2.7) Sedimentary structures are absent, but burrows, microfractures and the larger foraminifers are visible in core (Figure 2.7). Microfractures are infilled with calcite. Fractures are orientated between 30° and 90° to bedding planes. Phosphate grains are the only other grain visible in core, although this is rare.

Under plane polarised light and CL foraminifers are the dominant grains present. The foraminifera chambers are well preserved and infilled with non-ferroan calcite cement, suggesting infill was early immediately after or during deposition (Figure 2.7). Small zonations are seen within the cements that surround foraminifer’s chambers. Small pyrite frambooids are present in low quantities and are found on top of calcite cements. Electron
microscopy shows that the foraminiferal dominated packstone to grainstones are
dominated by isopachous calcite cement (figure 2.7). Quartz and clay minerals are present
but are a small component of this lithofacies.

XRD analysis shows that this lithofacies is dominated by calcite (89%). Quartz is the
second largest mineral component (~4%). Plagioclase and K-feldspar constitute ~2% and
~1% respectively with clay minerals ~5%. Over 90% of the clay present in the
foraminiferal dominated packstone to grainstones is mixed layer I/S. Kaolinite and illite
are the remaining clay minerals but are negligible in quantity. TOC values for this
lithofacies are ~0.3 wt%.

**Interpretation of the Foraminiferal dominated Packstone to Grainstone**

The foraminiferal dominated packstone to grainstones are present in the Middle and Upper
Eagle Ford Fmn. They occur above all the previous facies, displaying an overall carbonate-
content increasing sequence, then with a clay and organic-rich lithofacies (usually
lithofacies 3 or 5) overlying with a sharp basinal contact (figure 2.7), signalling the end of
parasequences (Friedman, 1964, Flugel, 2010). Thus, the foraminiferal dominated
packstone to grainstones are interpreted to be late highstand to early lowstand deposits that
were subject to oxygenated environments, typical of carbonate depositional environments

Water depth is difficult to interpret due to the absence of sedimentary structures in core
and thin section and that carbonate sediments often experience cementation during early
diagenesis. Cementation overprints sedimentary structures but can occur in shallow or deep
water. Due to the other lithofacies identified the foraminiferal dominated packstone to
grainstones are interpreted to be deposited in a shallow, high energy, oxic marine
environments (Bathurst, 1974, Flugel, 2010).
Figure 2.7. Foraminiferal dominated packstone to grainstone. A. Core photograph (J W Blumberg, depth 4129.59 ft) displaying sharp, well defined contacts with surrounding facies (red arrow). B. Thin section micrograph (Orts 7678.5) in PPL displaying benthic foraminifera (F) infilled with calcite cement. Recrystallised cements (CC) surrounding and within foraminifera are common. Some foraminifera shell walls remain intact (show in CL) (green arrow). Pyrite is also a common occurrence (yellow arrow). C. Thin section scan showing the light grey colour of the recrystallised foraminifera dominated packstone to grainstones. Some of the larger foraminifera can been seen with a hand lens. D. Thin section micrograph identical to the sample in C (Orts 772.70), in CL highlighting the foraminifera shells (yellow arrow), which remain dull luminescing compared to the brighter cements (CC) within and surrounding the foraminifera (F). E. SEM micrograph (Orts 7678.5) displaying the high quantity of calcite cements (CC). The remnants of foraminifera (F) shells are evident as they are replaced with clay quartz cements and leave display porosity. Green arrow denotes authigenic quartz cements surrounding a foram shell. Yellow arrow denotes illite infilling porosity around foraminifera. Red arrow denotes pyrite framboids on top of calcite cements.

2.3.8 Bentonite (Volcanic Ash)

Bioturbated bentonites (ash beds) are common throughout the Eagle Ford Fmn, especially in the Upper Eagle Ford Fmn (Figure 2.9). Bentonite beds are easy to distinguish in core, outcrop and thin section of the Eagle Ford Fmn, (Figure 2.8). The bioturbated bentonites are mainly green to brown in colour with thin strips of yellow to olive coloured material within the assemblage (Figure 2.8). Under ultraviolet light (UV) they fluoresce blue and yellow. The ash beds are variable in size (2cm-15cm thick). The beds are commonly bioturbated and have sharp contacts with lithofacies immediately below them (Figure 2.8). At the top, its common their contacts transition into other facies above them (gradational contact), although the majority of contacts remain sharp. Some ash beds display sediment disturbance with wavy ripples and cross beds. Notably in thin section, some ash beds are cemented with calcite (Figure 2.8).

XRD analysis shows that the mineralogy of the ash beds is; clay ~72%, calcite ~10%, pyrite ~18%, quartz ~5%, and plagioclase ~2%) and K-feldspar ~2%. The clay fraction is almost entirely mixed layer I/S (70%) with kaolinite composing the rest of the composition at 2%.

During the Late Cretaceous volcanism was prevalent in the Western Interior (Driskell et al., 2012, Elder, 1988, Nadeau et al., 1985). Ash beds are important because they are present throughout the formation, and are independent of spatial deposition mechanisms. The ash beds are also chronostratigraphically important as they mark an instantaneous period of deposition across the Eagle Ford Fmn (Elder, 1988). However, the preservation
of ash beds is variable as some display erosion surfaces and are truncated outcrop (Elder, 1988). In core they are near impossible to correlate over large distances due to a lack of spatial resolution, and the distance between cores locations.

Figure 2.8. Bentonite (Ash Bed). A. Outcrop photograph (GPS location, Lat: 29.4002, Long: -1012019) showing a significant bentonite bed present in the upper Eagle Ford (rock hammer for scale). B. Core photograph (Matthews J W 1-1, depth 4645.6ft) showing a bentonite bed (red box) surrounded by laminated foraminifera rich wackestones. C. Thin section scan (Orts 7746.40) displaying the clay smectite rich matrix bentonite with phosphatic skeletal material. D. Thin section micrograph of a sample in B Matthews J W 1-1, depth 4645.6ft), showing calcite cements (CC) and phosphatic skeletal material (red arrow) within the bentonites. Bentonites are rich in calcium carbonate and skeletal material. Smectite (Sm) is the main component of the bentonites.
2.3.9 Core Logs and Sequence Stratigraphy

Sequence Stratigraphy

Sequence stratigraphy is a method that divides strata into time-equivalent, related units linked, or associated with global sea level (Donovan, 2010, Grammer et al., 1993, Lehmann et al., 1999). Sequence stratigraphy is able to predict the distribution of facies within depositional systems, including sediment type, probable reservoir or source potential, geometry and lateral/vertical extent across a basin (Donovan, 2010). Sequence stratigraphy also recognises larger scale sequences (1st, 2nd and 3rd order sequences) are made up of stacked higher frequency (4th and 5th order) sequences. The major strengths of sequence stratigraphy is the ability to evaluate the direction of facies migration landward or seaward and the spatial variability of facies over time (Donovan, 2010, Dawson, 1997, Liro et al., 1994, Lehmann et al., 1999). However, ideally for a fully integrated 3D reservoir characterisation, sequence stratigraphy will combine extensive outcrop data and subsurface data (core, petrophysical logs and seismic) and ancient and modern analogs. Being able to combine the various datasets creates a vigorous model that can characterise and predict the quality and extent of a reservoir (Donovan, 2010, Dawson, 1997, Liro et al., 1994, Lehmann et al., 1999).

This study however, integrates a sequence stratigraphic model that does not use the ideal methods outlined previously, to create such a model. This study is limited to core data, a small volume of outcrop data from one location, but no petrophysical logs or seismic data. Furthermore, the cores that were logged, the distance between some is extensive, with one well 160km from the next nearest well. One well is also incomplete, with both the top and bottom missing. All scales and sequences were determined using the lithofacies scheme established through the analysis of five Eagle Ford Fmn cores (Matthews J L 1-1, Shell J A Leppard 1-H, J W Blumberg, W Bretchell and Shell Hay E D #1), undertaken at the Bureau of Economic Geology (BEG), Austin, Texas, USA (Figure 2.9).

The Eagle Ford Fmn is interpreted to represent a 2nd order supersequence event (Dawson, 1997, Liro et al., 1994). Within the supersequence 3rd (0.5 – 10Ma) and 4th (0.1 - 0.4Ma) order sequences and sequence cycles were identified in the five Eagle Ford Fmn cores (Figure 2.9). Each core, except for the Shell Hay E D #1, contains two 3rd order sequences (left side blue and orange triangles on core logs). These are superimposed onto the 2nd order supersequence (the Eagle Ford Fmn). However the sequence boundary is not
interpreted to be the Buda – Eagle Ford Fmn contact, but regression had already started somewhere in the Buda Limestone. The second 3rd order sequence is located in the top of the Lower Eagle Ford Fmn where there is a distinct transition in the lithology to less TOC, but carbonate rich (>60%) lithofacies that represent a transgressing systems track.

The Matthews J L 1-1 is the most westerly core (Figure 2.9). The core is 75ft long and displays the entire Eagle Ford Fmn, although the Lower Eagle Ford Fmn is truncated and considerably smaller than the Upper Eagle Ford Fmn section (Figure 2.10). The argillaceous mudstones are not observed in the Matthews J L 1-1. The weakly laminated mudstones with overlying recrystallised lime wackestones are the only lithofacies present in the Lower Eagle Ford Fmn (figure 2.9). This package of lithofacies (weakly laminated mudstones with overlying recrystallised lime wackestones) in the Lower Eagle Ford Fmn is associated with a 4th order sequence cycle, which contain 5th order sequences. The Matthews J L 1-1 mainly displays the Upper Eagle Ford Fmn, which mainly comprises of the laminated foraminferal rich wackestones, the skeletal wackestones to packstones and bioturbated lime mudstones to wackestones. At the very top of the core, the foraminiferal dominated packstone to grainstones are present up to the Eagle Ford Fmn – Austin Chalk contact (Figure 2.9). A change in lithofacies marks the transition from the Lower into the Upper Eagle Ford Fmn. The presence of the laminated foraminiferal rich wackestones above the recrystallised lime wackestones at 4676.80 ft marks the start of the Upper Eagle Ford Fmn where carbonate content increases significantly (figure 2.9). This lithofacies change at 4676.80 ft also denotes the start of the second 3rd order cycle in the Eagle Ford Fmn, which runs throughout the formation to the base of the Austin Chalk. In between these two boundaries are 11 4th order sequence cycles, which all contain 5th order cycles that alternate between with higher TOC, lower carbonate lithologies that transition into less TOC, higher carbonate lithofacies. This sequence pattern is present in all cores, in both the Lower and Upper Eagle Ford Fmn.

The Shell J A Leppard 1-H is approximately 160km east of the Matthews J L 1-1 core (Figure 2.9). The Shell J A Leppard 1-H is the longest core analysed at 139ft (figure 2.10). The J A Leppard 1-H displays the Lower Eagle Ford Fmn and the lower section of the Middle Eagle Ford Fmn. In the J.A Leppard 1-H, at the Buda – Eagle Ford Fmn contact are the argillaceous mudstones that transition into the weakly laminated mudstones, and then into the laminated foraminiferal-rich wackestones. Immediately above is a sharp contact back into the argillaceous mudstones and the same sequence begins, except some
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<tr>
<td>Road cut location on Highway 90</td>
<td></td>
<td>29.3797</td>
<td>-101.2038</td>
</tr>
</tbody>
</table>
Figure 2.9. Location map and table of GPS coordinates. Map denotes all Eagle Ford Fmn well locations across southern Texas (green circles) used in this study. The hollow yellow polygons denote the locations where the Eagle Ford Fmn outcrops in southern Texas. Red polygon denotes the general area of outcrops which were studied. Hollow blue polygons denote the Austin Chalk locations across southern Texas. Core logs from the Eagle Ford Fmn, 1) Matthews J L 1-1. 2) Shell Oil Co. J.A Leppard 1-H. 3) Jane W Blumberg B1. 4) Bretchell Wayne #1. 5) Shell Oil Co Hay, E.D Unit #1. The Shell Oil Co. J.A Leppard 1-H and the Shell Oil Co Hay, E.D Unit #1 display the Lower Eagle Ford Fmn. The Matthews J L 1-1 contains the entire Eagle Ford Fmn, but note the Lower Eagle Ford Fmn is truncated and not a full representation of the Eagle Ford Fmn. The Bretchell Wayne does contain the Lower Eagle Ford Fmn, but is truncated. The Jane W Blumberg represents the Upper Eagle Ford Fmn only. Third, fourth and fifth order sequences are identified in core and are shown by the blue, orange and red arrows respectively (see key).

sequences are now overlaid with a recrystallised lime wackestone (Figure 2.9). The argillaceous mudstones are limited to the very lower section of the Lower Eagle Ford Fmn, while the weakly laminated mudstones constitute the main volume of the Lower Eagle Ford Fmn (Figure 2.9). Climbing up through the stratigraphy, the weakly laminated mudstones decrease in volume and the laminated foraminiferal-rich wackestones become the dominant lithofacies. A distinct, large bed of recrystallised lime wackestone denotes the boundary of the Lower Eagle Ford Fmn, transitioning into the middle Eagle Ford Fmn. Fourth order sequence cycles are interpreted to cover a sequence of clay, TOC rich lithofacies transitioning into clay, TOC poor, carbonate rich lithofacies. In some of these sequences there was no evidence of 5th order sequences due to large consistent packages of lithofacies with little or no features present (Figure 2.9).

The Jane W Blumberg B1 is 70ft long and located on a similar longitude to the Shell J A Leppard 1-H core, but approximately 110km north (Figure 2.9). The Jane W Blumberg does not contain any argillaceous mudstone at the Buda – Eagle Ford Fmn contact. There is a small unit of weakly laminated mudstone with an overlying bioturbated lime mudstone to wackestone, which marks the end of the small and truncated Lower Eagle Ford Fmn and the start of the Upper Eagle Ford Fmn (Figure 2.10). The laminated foraminiferal-rich wackestones constitute the main volume of the Upper Eagle Ford Fmn with interbedded bioturbated lime mudstone to wackestones (Figure 2.9). The top section of the Upper Eagle Ford Fmn in the Jane W Blumberg B1 is entirely comprised of the foraminiferal dominated packstone to grainstones (Figure 2.9). The Jane W Blumberg B1 is a highly heterogeneous core, with a high number of 5th order sequence cycles present within 4th order sequences. The 5th order cycles are represented by small packages of lithofacies transitioning into the
next lithofacies which contains more carbonate and skeletal material. Bentonite (ash) beds are common in the J W Blumberg B1 core and often present in the bioturbated lime mudstones to wackestones.

The Bretchell Wayne #1 is 73ft long and is 40km south east of the J W Blumberg B1 well (Figure 2.10). The Bretchell Wayne#1 core is similar to the Matthews J L 1-1 and J W Blumberg B1 core where the Lower Eagle Ford Fmn is truncated, or a large proportion of it is missing. However, at the Buda – Eagle Ford Fmn contact in the Bretchell Wayne #1 the argillaceous mudstones are present, which transition into the weakly laminated mudstones (Figure 2.9). There is one sequence of argillaceous mudstone to weakly laminated mudstones that transition into the laminated foraminiferal rich wackestones, with a sharp contact in an overlying recrystallised lime wackestone (Figure 2.9). This sequence of lithofacies in the Lower Eagle Ford Fmn is interpreted to represent a fourth order sequence cycle, which was driving regression and relatively lower sea level. The recrystallised lime wackestone bed marks the end of the Lower Eagle Ford and the start of the Upper Eagle Ford Fmn. This boundary also represents the start of transgression which continues throughout the Upper Eagle Ford Fmn and into the overlying Austin Chalk (Figure 2.11). The Upper Eagle Ford Fmn comprises of the skeletal wackestones to packstones, bioturbated lime mudstones to wackestones and the foraminiferal dominated packstone to grainstone (Figure 2.9). There are frequent sequences of skeletal wackestones to packstones that transition into the bioturbated lime mudstones to wackestones and then often into the foraminiferal dominated packstone to grainstones. These sequences of lithofacies are interpreted to represent fourth and fifth order sequence cycles.

The Shell Hay E.D #1 is the shortest of the five cores analysed at 30ft long. The Shell Hay E D#1 core is furthest east (Figure 2.9 & 2.10). The Shell Hay E D#1only displays the Lower Eagle Ford Fmn. The Upper Eagle Ford Fmn is truncated, eroded away or simply was not covered in the coring process. The Shell Hay E.D Unit #1 does not contain any argillaceous mudstones (figure 2.9); however it does not contain the Buda – Eagle Ford Fmn contact, making it impossible to accurately place where the core present, belongs in the stratigraphy (figure 2.9). Like the Shell J.A Leppard 1-H core, the weakly laminated mudstones are the most common lithofacies in terms of volume. The weakly laminated mudstones transition into the laminated foraminiferal-rich wackestones with some sequences overlaid with a sharp contact into the recrystallised lime wackestones (Figure 2.9).
Figure 2.10. Core correlation between the 1) Matthews J L 1-1, 2) Shell Oil Co. J.A Leppard 1-H, 3) Jane W Blumberg B1, 4) Bretchell Wayne #1, 5) Shell Oil Co Hay, E.D Unit #1
It is difficult to determine if the lithofacies represent fourth or fifth order sequence cycles. Like the Shell J.A Leppard 1-H, the Shell Hay E.D #1 has large packages of the weakly laminated mudstones, which have no visible variation in bioclast content or variation in colour. After a large bed of the weakly laminated mudstones are deposited, they transition into the laminated foraminiferal rich wackestones. In total there are 7 fourth order sequence cycles in the Shell Hay E.D #1 core.

To summarise, the five cores display a general lithofacies distribution across the Eagle Ford Fmn (Figure 2.10). The Lower Eagle Ford Fmn mainly comprises of the clay-rich and organic-rich lithofacies (lithofacies 1, 2 and 3), (Figure 2.10 and Tables 2.0 and 2.1). The lower section of the Upper Eagle Ford Fmn (also known as the Middle Eagle Ford Fmn) mainly comprises of TOC bearing lithofacies (lithofacies 3, 5), however they contain significantly less TOC and more carbonate overall compared to the Lower Eagle Ford Fmn (figure 2.10 and Table 2.0). The Upper Eagle Ford Fmn is mainly comprises of carbonate-rich, TOC poor lithofacies (lithofacies 5, 6 and 7) and contributes little to hydrocarbon generation. Bentonite beds are present in all cores (Figure 2.9). However, bentonite beds are prevalent in the Upper Eagle Ford Fmn (Matthews J L 1-1, Bretchell Wayne #1 and Jane W Blumberg B1) (Figure 2.9 and 2.10).
2.4 Discussion

In this study, eight lithofacies were observed through the logging and the analysis of five Eagle Ford Fmn cores, along with optical and electron-microscopy analysis on 20µm cut thin sections. The lithofacies are characterised by; grain type, grain size, texture, colour, sedimentary structures, diagenetic features, biogenic content and TOC content. Cementation also influenced the facies association scheme as it is a common feature throughout the Eagle Ford Fmn. The lithofacies scheme is based on an idealised deepening upward lithofacies succession observed in the Eagle Ford Fmn.

The transition from clean water carbonates (Buda Limestone) to organic-rich mudstone (Eagle Ford Fmn) is interpreted to be a sequence boundary. The argillaceous mudstones, weakly laminated mudstones and foraminieral-rich wackestones are interpreted to have been deposited during a regressive systems tract or at a low stand (Figure 2.11). These types of sequence boundaries are associated with erosional surfaces and significant marine hiatuses, however there is no evidence for aerial exposure of the carbonate platform through sea level fall, (Schlager, 2005).

Core comparisons show that the argillaceous mudstones are not uniform across the entire Eagle Ford Fmn area (Figure 2.9). Thin sections sampled from cores in the west of the formation display less ripples and traction laminae. They suggest settling through suspension, suggesting a more pelagic environment. Samples from the northeast of the formation (Shell Hay E.D #1), display more clastic material, likely to be sourced from the East Texas Woodbine Delta and the rest of the interior (Dawson, 1997, Liro et al., 1994). Here the facies is comparably thick and overall thins towards the southwest.

The distribution of clay, organic-rich lithofacies (lithofacies 1, 2 and 3) in the Lower Eagle Ford Fmn (figure 2.9), suggest typical source rock depositional environments during the Late Cenomanian (Figure 2.11 and Figure 2.12). The argillaceous mudstones and weakly laminated mudstones are classic indicators of ideal source rock depositional environments due to their abundance of organic carbon, their colour and micro fossils present in the assemblage (Tyson, 2005, Ruofei et al., 2014, Kauffman, 1984, Wignall, 1994). Planktonic foraminifera and inoceramid bivalves are common and the only species present in the lower section of the Lower Eagle Ford Fmn lithofacies. Micro fossils such as planktonic foraminifera and inoceramid bivalves have been interpreted to indicate classic organic-rich source rocks deposition conditions; low energy, low oxygen content within the water...
Lithofacies that contain > 25% clay, contain TOC content > 4% are always present in core at the Buda – Eagle Ford Fmn contact (Figure 2.10). Despite some cores (Matthews J L 1-1, Jane W Blumberg B1, Bretchell Wayne #1) containing a truncated Lower Eagle Ford Fmn facies, the organic-rich lithofacies are present, albeit in smaller packages. The Shell J.A Leppard 1-H and the Shell Hay E.D #1wells are located near the boundary of Sligo Shelf and Karnes trough near the San Marcus Arch (Figure 2.0 & Figure 2.11). The Karnes trough and Sligo Shelf area experienced syndepositional faulting during the Late Cretaceous allowing for an increase in accommodation and focus the delivery of sediments that would eventually become the Eagle Ford Fmn. These geological features influenced the thickness of individual sequences/packages in the Shell J.A Leppard 1-H and the Shell Hay E.D #1 cores.

Figure 2.11, displays the interpreted conditions during the Late Cenomanian in the Western Interior Seaway (WIS). Core analysis of the Shell J.A Leppard 1-H and the Shell Hay E.D #1 cores in particular, suggests the organic-rich Lower Eagle Ford Fmn was deposited during regression and/or during a lowstand. During this period sea level was relatively low allowing the supply of clastic sediment to be transported further into distal environments (seawards) (Bohacs, 1998, Bohacs, 1990, Macquaker and Jones, 2002, Worden et al., 2000a). During the Late Cenomanian sufficient fine grained sediment (mainly smectite) was available to bury and preserve organic carbon (Scott, 1993, Scott, 1999, Schlanger and Jenkyns, 1976, Kauffman, 1984, Egger and Schwerd, 2008).

Throughout the periods of regression lowstands it is interpreted the Sligo and Edwards shelf reefs have acted like barriers and weakened the bottom water current from the boreal ocean in the north containing fresh nutrient-rich waters travelling south. A slowdown of upwelling is likely to have created water column stratification in the WIS. A lack of column mixing is likely to have exhausted oxygen content in the water column. An oxygen minimum zone is interpreted to be present in the WIS and could have created anoxic bottom waters around the Comanche platform and southern WIS. This OMZ and/or anoxic bottom waters favoured the preservation of organic material at the sediment water interface (Arthur and Sageman, 2004, Blakey, 2011, Wignall, 1994, Martin et al., 2012). During this period, lithofacies that contain high TOC (1. Argillaceous Mudstones. 2. Weakly
Laminated Mudstones. 3. Laminated Foraminieral-rich Wackestones) were deposited (Figure 2.11). The lower portion of the Lower Eagle Ford Fmn is interpreted to be a sequence boundary (lowstand) where clastic sediment to be transported further into distal environments (seawards) (Bohacs, 1998, Bohacs, 1990, Macquaker and Jones, 2002, Worden et al., 2000a). Proceeding this period of low sea level is an extensive period (2nd order) of transgression which, is reflected in the change of lithology (organic-rich, clay-rich lithofacies to organic-poor, carbonate domainated lithofacies) throughout the Eagle Ford Fmn.

Figure 2.11, displays the interpreted conditions during the Early Turonian after a substantial period of sea level transgression. During this period, clastic sediment supplied from the interior has retreated landward, with the lithofacies in the Eagle Ford Fmn gradually turning more carbonate-rich and transitioning through the middle Eagle Ford into the Upper Eagle Ford Fmn. Rising sea-level associated with transgression enabled input of fresh boreal deep waters from the north, as they were able to spill over the Sligo and Edwards Shelf, and rejuvenate column mixing, oxygenating the water column (figure 2.11) (Lowery et al., 2014, Corbett and Watkins, 2013, Kennedy et al., 2005). The reduction of clay content in the lithofacies and their distribution in the formation in the stratigraphy reflects the decrease in sediment supply throughout deposition. With a lack of sediment to bury organic matter and the presence of oxygen throughout the water column, organic matter preservation is shut down during the Turonian. This is reflected in the carbonate rich, TOC-poor lithofacies observed in the Upper Eagle Ford Fmn (Figure 2.11). The presence of benthic foraminifera observed in lithofacies in the upper section of the Lower Eagle Ford and Upper Eagle Ford suggests increased ocean turnover and a presence of oxygen in the deeper waters (Kauffman and Sageman, 1990, Kauffman, 1984) (Figure 2.11).
Figure 2.11. Generalised paleomap of the southern Western Interior Seaway (WIS) seabed, with sea level variation and physical and chemical processes. A. The WIS during the Late Cenomanian (99.6-94Ma) where sea level is relatively low but transgressing. Organic carbon preservation is prevalent due to dense saline Tethyan waters creating a stagnant, anoxic water column. Despite a stagnant water column, sufficient upwelling is able to bring enough nutrients to the photic zone for primary productivity. High preservation rates allows the majority of organic carbon to be preserved, despite initial productivity rates being relatively low. B. The WIS during OEA2 at the C-T boundary and lower Turonian. Sea level has risen due to transgression and is at its highest during the Cretaceous (sea level highstand). Fresh, boreal waters are drawn down the western side of the WIS and displace the dense, saline Tethyan waters, creating turnover increased upwelling and primary productivity. Water column turnover supplies oxygen to the bottom waters oxidising organic carbon. Despite higher levels of primary productivity in the surface waters, little of the organic material reaches the seafloor without being reduced. The ability of the basin to preserve organic matter is majorly weakened with carbonate the most common mineral precipitated at the seafloor. TOC is low.

Organic-rich source rocks and mudrocks are typically viewed as being indicators of low energy environments in the rock record, with high levels of primary productivity and low oxygen content in the water column or at the sediment water interface (Wignall, 1994, Tyson, 2005, Schlanger and Jenkyns, 1976, Donovan et al., 2012, Pederson and Calvert, 1990). Their abundance of organic carbon and clay with smaller quantities of other minerals give them their distinctive dark colour in core (and sometimes outcrop). Microfossils present in the rock assemblage can aid in the interpretation of deposition environments. For example, inoceramid bivalves thrive in oxygen depleted waters, indicating if they are present in the assemblage, that conditions during deposition were likely to be anoxic (Kauffman, 1984, Corbett and Watkins, 2013, Kauffman and Sageman, 1990, Kennedy et al., 2005).

The Eagle Ford Fmn is somewhat of an anomaly for source rocks deposited during the Late Cretaceous (Lowery et al., 2014, Corbett and Watkins, 2013). Prolific Late Cretaceous source rocks (La Luna Shale in Venezuela, Natih B in Oman and the Kazhdami in the Persian Gulf) were deposited during ocean anoxic event II (OEA2) (Ruofei et al., 2014). However in the Eagle Ford Fmn, the most organic rich lithofacies (the Lower Eagle Ford Fmn) were deposited before the onset of OEA2, with the organic poor lithofacies deposited during OEA2 (Figure 2.11 and 2.12).
Figure 2.12. Plot of Stratigraphic representation of mineralogical change with 4th and 5th order sequence cycles against clay content, carbonate (CaCO$_3$) content and total organic carbon (TOC). Clay-rich and TOC-rich lithofacies are present in the Lower Eagle Ford Fmn. Carbonate content increases climbing
throughout the stratigraphy while clay and TOC content drops. Ocean Anoxic Event 2 (OAE2) is interpreted (purple box) to have occurred during the Early Turonian where TOC-poor, carbonate-rich lithofacies in the Upper Eagle Ford Fmn.

A stagnant water column in the relatively low level (lowstand) Western Interior Seaway (WIS), typically driven by thermal and salinity variations and physical barriers created barriers blocking oxygen and nutrient mixing within the water column (Arthur and Sageman, 2004, Blakey, 2011, Wignall, 1994, Martin et al., 2012). This created a unique environment where organic matter was preserved throughout deposition and burial, creating the Lower Eagle Ford Fmn. In other regions around the world, organic matter was generally oxidised and degraded. With the onset of transgression and OEA2, the conditions allowing for organic carbon preservation were destroyed creating the Upper Eagle Ford deposited in oxic, normal marine conditions (Schlanger and Jenkyns, 1976, Lowery et al., 2014, Corbett and Watkins, 2013, Tyson, 2005, Pederson and Calvert, 1990, Al Balushi et al., 2013). Despite this, worldwide anoxia and organic matter preservation occurred in basins around the globe creating source rocks such as the La Luna Shale in Venezuela, Natih B in Oman.

The mechanisms that drove the onset of OAE2 are still poorly understood (Corbett and Watkins, 2013, Lowery et al., 2014, Elder, 1988, Elder and Kirkland, 1994). Heightened volcanic activity is thought to have increased global CO₂ concentrations in the atmosphere assisting in creating a “super greenhouse climate” (Blakey, 2011, Arthur and Sageman, 2004, Corbett and Watkins, 2013). As well as temperature and sea level rise during OAE2, an input of volcanic material falling to the surface waters of the WIS is thought to have created productivity blooms (Elder, 1988, Tyson, 2005, Pederson and Calvert, 1990). Volcanic activity is known to have occurred during the Late Cretaceous in the vicinity of the Eagle Ford Fmn due to the presence of numerous bentonite beds (volcanic ash) within the formation (Figures 2.8 and 2.9) (Donovan et al., 2012, Elder, 1988, Elder and Kirkland, 1994). Nutrients such as iron and phosphate are common within volcanic ash and act as a fertiliser on the sea surface (Nadeau et al., 1985, Elder, 1988, Blakey, 2011). Primary productivity within the photic zones was therefore likely to be higher in the Turonian compared to the Late Cenomanian due to the increased distribution of bentonite beds observed in the Upper Eagle Ford Fmn (figure 2.9) (Tyson, 2005, Pederson and Calvert, 1990, Elder, 1988). An effect of increased primary productivity rates increases the quantity of trophic level predators in the surface waters (such as Coccolithophores), which
feed on the primary producers (Corbett and Watkins, 2013, Lowery et al., 2014, Silva and Duarte, 2015, Denne et al., 2014). Their shells fall to the sea floor and additional carbonate is precipitated at the sediment water interface (Silva and Duarte, 2015). This process is a potential source of additional carbonate which is seen distrusted throughout the carbonate rich, TOC-poor lithofacies of the Upper Eagle Ford Fmn.

Sequence Stratigraphy

Stacking patterns of carbonates and organic-rich, carbonate-rich formations like the Eagle Ford Fmn are frequently overlooked as they show no evidence of subaerial exposure (Miall, 2010, Grammer et al., 1993). Therefore they do not show a carbonate platform that has been abandoned due to a fall in sea-level. Despite this the lithofacies cyclicity observed in the Eagle Ford Fmn is characteristic of periplatform carbonates that record sea-level fluctuation through carbonate production (Goldhammer et al., 1990, Goldhammer and Johnson, 2001, Grammer et al., 1993). In this study, sequences were determined based on a lithofacies type present and a landward/seaward shift following the stacking pattern of lithofacies present in the lithofacies scheme (Table 2.3).

The Eagle Ford Fmn-Austin Chalk records a 2nd order sequence (Donovan, 2010, Hentz and Ruppel, 2010, Liro et al., 1994). Within the 2nd order sequence there are two interpreted 3rd order sequences from the five cores analysed. The author stresses that other 3rd order sequences could be present within the formation but could not be clarified since every core was missing a section and/or was truncated. The first 3rd order sequence represents the organic-rich, clay-rich lithofacies which are distributed in the lower section, with the second sequence in the upper section, which represents a decrease in TOC with increased carbonate content. The boundary between the two 3rd order sequences is marked by a large limestone bed which separates the Lower and Upper Eagle Ford Fmn (Shell J A Leppard 1-H core, Figure 2.9).

Third order sequences are composed of higher frequency 4th order sequences. Fourth order sequences are influenced by the Milankovitch cycles (eccentricity, obliquity and precession), which manufacture varying amounts of solar radiation received by earth. These three cycles contribute to climate change and drive high frequency sea level fluctuations by glacioeustatic variation (Dawson, 1997, Donovan, 2010, Goldhammer et al., 1990).
A total of 34 4th order sequence cycles were identified across the five Eagle Ford Fmn cores (Figure 2.9). Each cycle represents a deepening upward sequence that follow the idealised lithofacies pattern illustrated in table 2.3. The 4th order sequence cycles are bound by a surface where shallower water lithofacies (argillaceous mudstones, weakly laminated foraminiferal mudstones) transition upward into deeper water lithofacies, such as the recrystallised lime wackestones (top of sequence). Fourth order (higher frequency) cycles represent individual packages in the Eagle Ford Fmn, from high TOC, clay rich rocks to low TOC carbonate rich rocks. It is difficult to determine regional consistency between cores regarding the number of 4th order sequence cycles present within each 3rd order sequence due to core coverage and the vast distances between some of them (Figure 2.0). It is impossible to correlate the number of sequences present in the Lower Eagle Ford Fmn due to the Shell J A Leppard 1-H only displaying the lower section in its entirety. The Shell Hay E.D #1 only displays a section of the Lower Eagle Ford Fmn and parts are missing. However in the Upper Eagle Ford Fmn, despite vast distances between the Matthews J L 1-1 in the west of formation and the Jane W Blumberg B1 and Bretchell Wayne #1 in the north east, there is regional correlation within the 4th order sequence cycles. In the Matthews J L 1-1 and Jane W Blumberg B1 there are 5 4th order sequence cycles. The Bretchell Wayne #1 also contains 5 or 6. It is difficult to be certain due to some core missing. The thickness of each 4th order sequence is also consistent within the three cores (Figure 2.9 and 2.10). In the Shell J A Leppard 1-H core, 4th order sequences (packages) are much larger than the other cores. This is a probable reflection of where the Shell J A Leppard 1-H is located, near the Edwards shelf reef and Karnes trough. Here the influence of allocyclic and autogenic processes such as; syndepositional faulting, subsequent accommodation development and turbidity flows created thicker packages in this area.

There are 109 5th order sequence cycles identified across the five cores analysed (Figure 2.9). The distribution and thickness of 5th order sequences lack consistency seen in the 3rd and to an extent, the 4th order sequences in the Upper Eagle Ford Fmn. There is no distinct pattern or reason for variation in thickness of the sequences. Although, in the Shell J A Leppard 1-H and Shell Hay E.D #1 and J W Blumberg B1 there is evidence to suggest sequences generally become less frequent, but thicker (Figure 2.9). The lack of correlation and regional consistency between the cores are likely to be related to high frequency sea level variation but also local conditions, such as sediment supply, seafloor morphology and
carbonate production (Goldhammer et al., 1990, Goldhammer and Johnson, 2001, Donovan, 2010).

The absence of 5th order cycle correlation between cores prevents them being used to correlate high frequency cycles across the Eagle Ford Fmn. High frequency cycles (4th and 5th order sequence cycles) are generally meter scaled (3ft) and are described as parasequences that consist of a number of units (lithofacie) that make up an individual deepening upward sequence. The sequence then repeats itself with an abrupt fall in sea-level (Goldhammer et al., 1990, Grammer et al., 1993). Identification of these packages and cycles is essential for reservoir characterisation, prediction and modelling as they often represent fluid flow in carbonate reservoirs (Bombardiere and Gorin, 2000, Droste and van Steenwinkel, 2004, Goldhammer et al., 1990). They also enhance the predictability of sedimentary packages/units, reservoir/source/seal potential, their geometry and the lateral/vertical extent of each in the subsurface (Goldhammer et al., 1990, Dawson and Almon, 2010, Donovan, 2010, Driskell et al., 2012).

2.5 Conclusions

Through outcrop, petrographical (PPL, CL and SEM) and geochemical analysis (XRD and Rock Eval), eight lithofacies were identified within the Eagle Ford Fmn. The lithofacies vary in mineral composition, organic content, faunal content, sedimentary structures and vary in unit size (from decimetre to metre scale). The lithofacies display overall coarsening upward (due to biogenic content), or increase in carbonate content upward sequences. This observation is particularly notable in the Lower Eagle Ford Fmn.

The distribution of high TOC, clay rich lithofacies present in the Lower Eagle Ford Fmn, and TOC, clay-poor, carbonate dominated lithofacies present in the Upper Eagle Ford Fmn suggests a significant change in depositional conditions during deposition. This has impacted faunal content, sedimentation rates and geochemistry of the water column. Such changes had a detrimental effect on organic carbon preservation. These observations linked with sequence stratigraphic analysis suggest the Eagle Ford Fmn was initially deposited in relatively low sea levels during regression or a possible low stand. Overall transgression (2nd and 3rd order) with periods of varying sea-level change (4th and 5th order sequences) created individual lithological units within parasequences or “genetic units”. These parasequences display a deepening upward trend where TOC and clay content decrease,
while carbonate content increases (Figure 2.12). Fourth order, deepening upward sequences mirror the entire transition of the formation, where the TOC-rich Lower section transitions into the TOC-poor carbonate-rich Upper Eagle Ford Fmn and eventually to the Austin Chalk (2\textsuperscript{nd} and 3\textsuperscript{rd} order cycles) (Figure 2.12).

Therefore the Lower Eagle Ford Fmn represents an anoxic, marine environment with sufficient clastic sedimentation transported seaward to preserve and bury organic material before the onset of OAE2. In contrast the Upper Eagle Ford Fmn represents an environment experiencing rapid transgression with increasing sea levels inducing local ocean turnover, increased oxygenation of the water column, and a landward shift of clastic sedimentation, which equated to the destruction of organic matter and the production of cleaner carbonate lithologies during OEA2.
3. Diagenesis in the Eagle Ford Formation
3.1 Introduction

Organic-rich-mudstones are an important sink of carbon in the global carbon-cycle and are the source of hydrocarbons in petroleum systems. Currently, they are targeted as reservoirs in unconventional shale-gas and shale-oil plays (Taylor and Macquaker, 2014, Macquaker et al., 2014, Aplin and Macquaker, 2011, Donovan et al., 2012).


The precipitation of early cements followed by compaction creates low permeabilities, meaning the mobility of solutes in pore fluids are limited in mudstones (Macquaker et al., 2014). Equilibrium driven diffusion reactions dominate later, deeper burial diagenesis where pervasive cements are precipitated (Laubach et al., 2010, Curtis, 1977, Macquaker et al., 1997). These reactions are key to mudstone composition and reservoir characterisation. Carbonate and silicate cements (in particular carbonate cements in the Eagle Ford Fmn), infill porosity and ensures low permeability’s in mudstones (Laubach et al., 2010).

In mud dominated, lower energy deposition environments, diagenetic processes and the products that originate from them are controlled by the availability of four main products. 1) The availability of oxidants within the pore waters (diffused from the overlying water
mass). 2) The availability of mineral oxidants and sesquioxides, such as iron and manganese (these are delivered in solid phase to the sea floor from terrestrial sources). 3) The availability of reductants such as organic carbon, methane, sulphate, H$_2$S and algae to be used by microbes for respiration. 4) The availability of pore water buffering materials such as calcium carbonate and free silicate from Opal A dissolution (Macquaker et al., 1997, Coleman and Raiswell, 1995, Coleman, 1985, Coleman, 1993, Macquaker et al., 2014, Moore et al., 2004). The availability of certain oxides and reducers greatly influences the characteristics of a mudstone. This is important to petroleum geologists because it has profound effects on source rock quality (TOC, HI, PI), and producability in an unconventional sense (Macquaker et al., 2014, Dawson and Almon, 2010, Davies et al., 2012). The latter is controlled by the mudstones physical and mechanical properties (porosity, permeability and ductility) (Davies et al., 2012, Martin et al., 2011). Carbonate and silicate cements attribute most to physical and mechanical properties because they can close primary porosity and significantly reduce permeability (Thyberg et al., 2010, Curtis, 1977, Schieber et al., 2000, Taylor and Macquaker, 2014, Macquaker et al., 2014, Al Balushi et al., 2013). However, depending on the cement type, cementation can make a rock more brittle making it ideal for stimulation via hydraulic fracturing. The type of organic material and how efficiently it is preserved and buried controls how much petroleum is generated and expelled. This of course is also intrinsically linked to organic matter type, burial history and thermal maturity (Pepper and Corvit, 1995, Donovan et al., 2012, Dawson, 1997).

No thorough diagenetic studies have been undertaken on the Eagle Ford Formation (Fmn) in south Texas, USA. This chapter will answer how diagenesis throughout the Eagle Ford (Fmn) has effected mineralogical composition, geochemical composition and physical properties (porosity). The main focus is; 1) identifying diagenetic processes and their products, 2) paragenetic histories and the role diagenesis has played in lithofacies development in the Eagle Ford Fmn.
3.2 Materials and Methods

78 thin sections were prepared (cut at 20µm) at Statoil ASA, Bergen. 23 of these thin sections were from the Matthews J L 1-1, Shell J A Leppard 1-H, J W Blumberg, W Bretchell and Shell Hay E-D 1 cores from Chapter 2 Lithofacies of the Eagle Ford Fmn. The remaining 55 thin sections are from unobserved cores, Wagner Bros Inc 11, Lloyd Hurt 1 and H-P Orts 2 (Figure 3.0). The 55 thin sections were sampled by Statoil personnel from the Bureau of Economic Geology (BEG) in Austin, Texas in 2011. The cores they obtained the material from were not available to observe or sample further.

All thin sections were scanned using a flatbed scanner (Cannon CanoScan 5600F), generating high quality whole thin section images. Each thin section was then analysed under low to medium resolutions (10⁻³ to 10⁻⁴ m scale) under transmitted light (TL) in both plane polarised light (PPL) and cross polarised light (XPL) using a Nikon Optiphot2-Pol petrographic microscope. Examination of the thin sections under XPL was of little help due to the nature of high interference colours when the thin section is cut too thin (20µm).

On top of the microscope viewing the thin sections was a Jenoptik jena-07739 digital camera allowing photomicrographs to be taken. A CITL Cathodoluminescence Unit (Model CCL 8200 mk3) was used alongside an Olympus BH-2 petrographic microscope, with both utilising a digital camera (Jenoptik jena-07739) to capture micrographs in CL and PPL. Operating conditions for the CL were approximately 20kv (cathode voltage), 300 µA electron beam current and 0.2 torr vacuum.

Bulk XRD analysis was also undertaken to help identify and quantify the minerals present in each lithofacies. Qualitative and qualitative mineral composition of 44 Eagle Ford Fmn bulk rock samples was determined by an X-ray diffractometer (XRD). This analysis was undertaken at The University of Manchester and at Statoil ASA.

Rock-Eval analysis was undertaken on 22 samples to obtain TOC (%Wt). These were obtained from samples extracted from the five cores logged at the BEG, and additional data available from the BEG but were able to be correlated to a lithofacies due to the depth given. The samples extracted during the core logging were analysed at Statoil ASA, Bergen. Six core plugs were extracted from the outcrops using a rock-bore drill. These plugs were used for He-porosimetry measurements to obtain total porosities. The plugs
were extracted from relatively fresh outcrop, where weathering and erosion was minimal. Analysis was undertaken at Statoil ASA, Bergen.

Petrographic, diagenetic and compositional information were obtained from these techniques. After TL and CL investigations 38 thin sections were selected and carbon coated for electron l analysis to examine the composition and diagenetic fabrics and other constitutes at higher resolution (10^{-5} to 10^{-6} m scale). This was done using a Philips XL30 ESEM-FEG fitted with an EDAX Genesis EDS system. The microscope was operated at 15kV and at 10mm working distance which allowed the viewing of back scattered electron, (BSE imagery), and energy dispersive spectrometry, (SE).

Stable carbon and oxygen isotope analysis was performed on (whole rock) 29 samples that were analysed by XRD. All 29 samples were subject to a cold methanol: dichloromethane (1:9 solvent) extraction at room temperature using an ultra-sonic water bath to remove the organic content. To separate the sample and solvent they were centrifuged and then left in a fume cupboard over night to dry and let any excess solvent to evaporate. The samples were inserted into a VG SIRA-12; gas sourced mass spectrometer (MS) in the University of Liverpool Stable Isotope Laboratory, UK. Here, $^{13}$C/$^{12}$C and $^{18}$O/$^{16}$O ratios were measured. All results and ratios are presented by the standard delta ($\delta$) as parts per mill (‰) from the Vienna Pee Dee Belemnite (VPDB) international standard.

An additional clay mineral dataset was provided by Statoil ASA from their joint venture well, Statoil/Talisman-1. This dataset extends throughout the entire Eagle Ford Fmn, from the Buda Limestone contact to the overlying Austin Chalk. However, while Statoil and Talisman were happy to provide the dataset for this project, there is no detail to the log. There is no indication how long the well is, no depths indicated, and no stratigraphic markers. While there is a breakdown of individual clay minerals present, there is no indication of total quantities, just ratios and therefore does not give an accurate indication of clay content at any particular depth. The location of the Statoil/Talisman-1 well is indicated in Figure 3.0.
<table>
<thead>
<tr>
<th>Lithofacies</th>
<th>Main minerology (XRD)</th>
<th>Colour</th>
<th>Main Grains Present</th>
<th>Sedimentological Characteristics</th>
<th>TOC (wt%)</th>
<th>Φ %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Avg %</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(n=3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(n=1)</td>
<td></td>
</tr>
<tr>
<td>1 Argillaceous Mudstone</td>
<td>29 22 - 36 (n=6)</td>
<td>Black to</td>
<td>Mixed layer I/S, Kaolinite/chlorite, planktonic</td>
<td>Faintly laminated- sometimes massive. Ripple laminae are common. Some burrowing is present but</td>
<td>5</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>very dark</td>
<td>globigerinid foraminifera</td>
<td>extremely rare.</td>
<td>3.35-6.49</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>green/brown</td>
<td></td>
<td></td>
<td>(n=3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(n=1)</td>
<td></td>
</tr>
<tr>
<td>2 Weakly laminated Mudstone</td>
<td>47 31-55 (n=8)</td>
<td>Black</td>
<td>Mixed layer I/S. Kaolinite/chlorite, planktonic</td>
<td>Thin (sub mm) planar but truncated laminae. Some are wavy but are only present at the bottom of</td>
<td>6.5</td>
<td>9.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>planktonic (globigerinid) foraminifera.</td>
<td>packages where they transition from the Argillaceous Mudstones Contain sharp or erosive contacts.</td>
<td>4.21-7.84</td>
<td>8.5-10.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(n=3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(n=2)</td>
<td></td>
</tr>
<tr>
<td>3 Laminated Foraminifera-rich</td>
<td>62 52-76 (n=7)</td>
<td>Medium to</td>
<td>Mixed layer I/S. Globigerinid planktonic foraminifera and</td>
<td>Planar laminated. Laminations consist of foraminifers. Some laminae resemble ripples, although this</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Wackestones (crystalline)</td>
<td></td>
<td>dark Grey</td>
<td>benthic foraminifera. Calcite cements. Kaolinite</td>
<td>is rare. Burrowing is present.</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 Recrystallised Lime</td>
<td>90 79-94 (n=8)</td>
<td>Light Grey</td>
<td>Recrystallised carbonate cements cements</td>
<td>Highly cemented with calcium carbonate. Crystalline texture. Cement grains in size from 20-100µm.</td>
<td>0.06-0.08</td>
<td>3.76</td>
</tr>
<tr>
<td>Wackestones (crystalline)</td>
<td></td>
<td></td>
<td></td>
<td>Fractures are infilled and closed with carbonate, though rare.</td>
<td>(n=4)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(n=2)</td>
<td></td>
</tr>
<tr>
<td>5 Skeletal Wackestone to</td>
<td>73 65-86 (n=6)</td>
<td>Medium to</td>
<td>Fragmented Inocerarum bivalves, Globigerinid</td>
<td>Strongly laminated and bedded. Cross laminae and imbricated bedding. Scour and truncated laminae</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>Packstones</td>
<td></td>
<td>light grey</td>
<td>Foraminifera, Peloids, phosphate grains. Fish bones</td>
<td>surfaces. Skeletal fragments most dense at base of units and become more rare- fining up.</td>
<td>0.29-7.29</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>and teeth.</td>
<td></td>
<td>(n=3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 Bioturbated Lime mudstone to</td>
<td>84 76-88 (n=6)</td>
<td>Dark grey to</td>
<td>Bivalves, foraminifera, radiolarians and unidentifiable</td>
<td>Bioturbated. Moderately recrystallised with calcium carbonate. Fractures are infilled and closed</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>Wackestone</td>
<td></td>
<td>light grey</td>
<td>skeletal material.</td>
<td>with carbonate, though rare. Some skeletal fragments are calcified, some are phosphotosed, though</td>
<td>0.64-2.45</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>rare.</td>
<td>(n=4)</td>
<td></td>
</tr>
<tr>
<td>7 Foraminiferal dominated</td>
<td>89 85-98 (n=4)</td>
<td>Light grey</td>
<td>Carbonate cements. Benthic foraminifera, unidentifiable</td>
<td>Recrystallised. Fractures are infilled with calcium carbonate. Commonly interbedded with skeletal</td>
<td>0.3</td>
<td>2.6</td>
</tr>
<tr>
<td>Packstone to Grainstone</td>
<td></td>
<td></td>
<td>skeletal material</td>
<td>wackestones and packstones.</td>
<td>0.18-0.30</td>
<td>(n=3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(n=1)</td>
<td></td>
</tr>
<tr>
<td>8 Bentonite (Volcanic Ash)</td>
<td>10 (n=1)</td>
<td>Green-grey-</td>
<td>Bioclasts, large skeletal fragments and teeth.</td>
<td>Commonly massive, although some beds do contain planar laminae. Heavily bioturbated.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>yellow</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.0 Summary of the mineralogical composition from XRD of the eight lithofacies observed in the Eagle Ford Fmn. 1) Argillaceous mudstones (7 samples). 2) Weakly Laminated Mudstone (11 samples). 3) Laminated Foraminifera rich Wackestones (9 samples). 4) Recrystallised Lime Wackestones (8 samples). 5) Skeletal Wackestone to Packstone (11 samples). 6) Bioturbated Lime Mudstone to Wackestone (7 samples). 7) Foraminiferal dominated Packstone to Grainstone (4 samples). 8) Bentonite, Volcanic Ash (1 sample)
### Lithofacies: Bulk Stable-Isotopic Compositions

<table>
<thead>
<tr>
<th>Sample/Core</th>
<th>Depth (ft)</th>
<th>δ13C ‰</th>
<th>δ18O ‰</th>
<th>Lithofacies</th>
</tr>
</thead>
<tbody>
<tr>
<td>ORTS-34</td>
<td>7755</td>
<td>0.34</td>
<td>-6.42</td>
<td>Argillaceous Mudstones</td>
</tr>
<tr>
<td>HAY-41</td>
<td>13827.50</td>
<td>-0.37</td>
<td>-6.90</td>
<td>Argillaceous Mudstones</td>
</tr>
<tr>
<td>HAY-42</td>
<td>13828.50</td>
<td>0.70</td>
<td>-6.94</td>
<td>Argillaceous Mudstones</td>
</tr>
<tr>
<td>ORTS-37</td>
<td>7752</td>
<td>0.10</td>
<td>-6.64</td>
<td>Weakly Laminated Mudstone</td>
</tr>
<tr>
<td>HAY-36</td>
<td>13822.58</td>
<td>0.80</td>
<td>-6.94</td>
<td>Weakly Laminated Mudstone</td>
</tr>
<tr>
<td>HAY-37</td>
<td>13823.58</td>
<td>0.20</td>
<td>-6.96</td>
<td>Weakly Laminated Mudstone</td>
</tr>
<tr>
<td>HAY-39</td>
<td>13825.50</td>
<td>0.62</td>
<td>-7.29</td>
<td>Weakly Laminated Mudstone</td>
</tr>
<tr>
<td>HURT-151</td>
<td>7277.22</td>
<td>1.10</td>
<td>-6.94</td>
<td>Weakly Laminated Mudstone</td>
</tr>
<tr>
<td>HURT-159</td>
<td>7287.33</td>
<td>1.33</td>
<td>-7.89</td>
<td>Weakly Laminated Mudstone</td>
</tr>
<tr>
<td>ORTS-85</td>
<td>7703</td>
<td>0.11</td>
<td>-5.74</td>
<td>Laminated Foraminiferal rich Wackestones</td>
</tr>
<tr>
<td>ORTS-100</td>
<td>7688</td>
<td>0.95</td>
<td>-4.75</td>
<td>Laminated Foraminiferal rich Wackestones</td>
</tr>
<tr>
<td>HAY-21</td>
<td>13724.50</td>
<td>-1.76</td>
<td>-4.77</td>
<td>Laminated Foraminiferal rich Wackestones</td>
</tr>
<tr>
<td>GETTY HURT-164</td>
<td>7293.83</td>
<td>-1.54</td>
<td>-4.87</td>
<td>Laminated Foraminiferal rich Wackestones</td>
</tr>
<tr>
<td>B5</td>
<td>outcrop</td>
<td>-3.29</td>
<td>-4.27</td>
<td>Recrystallised Lime Wackestones</td>
</tr>
<tr>
<td>B4-1V</td>
<td>outcrop</td>
<td>-6.96</td>
<td>-4.20</td>
<td>Recrystallised Lime Wackestones</td>
</tr>
<tr>
<td>B3</td>
<td>outcrop</td>
<td>-8.61</td>
<td>-3.34</td>
<td>Recrystallised Lime Wackestones</td>
</tr>
<tr>
<td>B4-3H</td>
<td>outcrop</td>
<td>-9.22</td>
<td>-3.34</td>
<td>Recrystallised Lime Wackestones</td>
</tr>
<tr>
<td>Hurt-168</td>
<td>7298.72</td>
<td>-10.16</td>
<td>-4.91</td>
<td>Recrystallised Lime Wackestones</td>
</tr>
<tr>
<td>Location</td>
<td>Depth (m)</td>
<td>V1</td>
<td>V2</td>
<td>Description</td>
</tr>
<tr>
<td>---------------</td>
<td>-----------</td>
<td>-----</td>
<td>-----</td>
<td>-----------------------------------</td>
</tr>
<tr>
<td>ORTS-96</td>
<td>7692</td>
<td>-0.28</td>
<td>-4.65</td>
<td>Skeletal Wackestones to Packstones</td>
</tr>
<tr>
<td>HAY-27</td>
<td>13813.50</td>
<td>-0.57</td>
<td>-6.72</td>
<td>Skeletal Wackestones to Packstones</td>
</tr>
<tr>
<td>Hurt-136</td>
<td>7257.72</td>
<td>0.56</td>
<td>-5.39</td>
<td>Skeletal Wackestones to Packstones</td>
</tr>
<tr>
<td>ORTS-99</td>
<td>7689</td>
<td>-0.27</td>
<td>-4.75</td>
<td>Bioturbated Lime Mudstone to Wackestone</td>
</tr>
<tr>
<td>ORTS-94</td>
<td>7694</td>
<td>-0.49</td>
<td>-4.53</td>
<td>Bioturbated Lime Mudstone to Wackestone</td>
</tr>
<tr>
<td>ORTS-95</td>
<td>7693</td>
<td>-0.34</td>
<td>-5.35</td>
<td>Bioturbated Lime Mudstone to Wackestone</td>
</tr>
<tr>
<td>GETTY HURT-164</td>
<td>7293.83</td>
<td>-1.54</td>
<td>-4.87</td>
<td>Bioturbated Lime Mudstone to Wackestone</td>
</tr>
<tr>
<td>GETTY HURT-155</td>
<td>7282.00</td>
<td>-2.40</td>
<td>-4.54</td>
<td>Recrystallised Foram dominated Packstone to Grainstone</td>
</tr>
<tr>
<td>GETTY HURT-162</td>
<td>7291.33</td>
<td>-3.56</td>
<td>-5.47</td>
<td>Recrystallised Foram dominated Packstone to Grainstone</td>
</tr>
<tr>
<td>GETTY HURT-166</td>
<td>7296.28</td>
<td>-3.63</td>
<td>-5.41</td>
<td>Recrystallised Foram dominated Packstone to Grainstone</td>
</tr>
<tr>
<td>ORTS-93</td>
<td>7695</td>
<td>-1.34</td>
<td>-4.42</td>
<td>Recrystallised Foram dominated Packstone to Grainstone</td>
</tr>
</tbody>
</table>
Figure 3.0. A. Cross-plot showing bulk stable carbon and oxygen isotopic compositions of lithofacies 1-7 (table 3.0). The organic rich, clay rich lithofacies (argillaceous mudstones, weakly laminated mudstones and laminated foraminiferal-rich wackestones), contain isotopically heavy δ¹³C values and isotopically light δ¹⁸O values. Coccolith fragments are the main carbonate component in these lithofacies, which have been recrystallised during later diagenesis creating more negative δ¹⁸O values. The laminated foraminiferal-rich wackestones contains more diagenetic carbonate precipitated in foraminifer’s chambers, resulting in less negative δ₁⁸O values. The Skeletal Wackestones to Packstones contain more carbonate than the laminated foraminiferal-rich wackestones, however their bulk compositions are skewed by the high skeletal fragment content, creating an overall marine derived signature (δ¹³C values; δ¹³C values generally become more negative indicating sufficient diagenetic carbonate is present in the bioturbated lime mudstone to wackestones. Bulk isotopic values indicate diagenetic carbonate interpreted to be precipitated from aerobic oxidation of organic matter and sulphate reduction dominates the composition of the recrystallized lime wackestones and recrystallized foraminiferal dominated packstones to grainstones. The recrystallised foraminiferal dominated packstones to grainstones still contain a high quantity of original shell material. This explains why their δ¹³C values are not as negative as the concretions, which contain no shell or skeletal material. B. Location map and table of GPS coordinates. Map denotes all Eagle Ford Fmn well locations across southern Texas (green circles) used in this study. The hollow yellow polygons denote the locations where the Eagle Ford Fmn outcrops in southern Texas. Red polygon denotes the general area of outcrops which were studied. Hollow blue polygons denote the Austin Chalk locations across southern Texas.
3.3 Mineral Composition and Diagenetic Processes

The Late Cretaceous Eagle Ford Fmn is a highly variable reservoir, with calcite ranging from 29-90%, clay minerals 4-44%, quartz 4-22% and organic carbon (range; 3.25-7.84%wt, average; 5.16%) (Table 3.0 and Figure 3.1). The first three lithofacies in the idealised lithofacies scheme (argillaceous mudstones, weakly laminated mudstones and laminated foraminiferal-rich wackestones) are compositionally similar, and share similar diagenetic processes, but with some differences and varying quantities of products precipitated (Table 3.0). These three lithofacies are generally clay and TOC-rich with calcite content ranging from 29-76%. The argillaceous mudstones, weakly laminated mudstones and laminated foraminiferal-rich wackestones are predominantly observed in the Lower Eagle Ford Fmn (Figure 3.1).

The recrystallised lime wackestones, are thoroughly described diagenetically in the next chapter, but will be described briefly here in the second group of lithofacies with the skeletal wackestones to packstones, bioturbated lime mudstones to wackestones and recrystallised foraminiferal dominated packstone to grainstones.

The skeletal wackestones to packstones, bioturbated lime mudstones to wackestones and recrystallised foraminiferal-rich packstones to grainstones are considerably different compared to the first three lithofacies (argillaceous mudstones, weakly laminated mudstones and laminated foraminiferal-rich wackestones), in the idealised lithofacies scheme (Table 3.0). The skeletal wackestones to packstones, bioturbated lime mudstones to wackestones and recrystallised foraminiferal-rich packstones to grainstones contain lower TOC values overall (range; 0.18-7.29, average; 1.4), contain higher carbonate content and lower clay mineral content (Figure 3.1).

The differences and similarities between the lithofacies will be summarised in a series of paragenetic sequence charts at the end of this section (figures 3.6 and 3.7). The bulk of this section will describe the diagenetic processes and products precipitated in the Eagle Ford Fmn.
Figure 3.1. Plot of an idealised Eagle Ford Fmn core log, containing the entire formation with its idealised lithofacies scheme (see chapter 2; Lithofacies of the Eagle Ford Fmn) with: clay content, calcium carbonate content, total organic carbon (TOC), pyrite content, quartz content and levels of bioturbation throughout the formation.
3.3.1 Calcite and Pyrite

Calcite content is observed in varying quantities throughout the Eagle Ford Fmn (Figure 3.1). Calcite is commonly observed infilling foraminfera (planktonic and benthic), throughout the Eagle Ford Fmn (figure 3.2). Foraminifera tests infilled with calcite are well preserved in thin section. Calcite is also observed as cements (including dolomite under SEM), mainly surrounding and replacing biogenic debris such as foraminifers, coccolith tests, bivalves and other skeletal debris (figure 3.1). The replacement of skeletal debris is particularly common in the carbonate-rich lithofacies (5-7). In lithofacies 1 and 2, SEM analysis reveals the main constitute of calcite is coccolith debris within the micritic matrix (figure 3.1 and 3.2). The distribution of calcite changes throughout the lithofacies with an increasing amount observed as equant authigenic cements in the carbonate-rich lithofacies. In lithofacies 7 over 85% of the composition is calcite, with 95% of it observed as blocky, equant cements within and surrounding benthic foraminifera (figure 3.1).

Cathodoluminescence (CL) shows foraminifera to contain infilling non-zoned, non-ferroan calcite cements that are brighter than the original shell material (biogenic debris) in lithofacies 1 and 2. Some foraminifera in lithofacies 3 contain slightly zoned non-ferroan calcite cements, although this is rare. In the organic-rich lithofacies (1, 2 and 3), CL shows the matrix to be dull (dark red to brown) (figure 3.1). Calcite within the micritic matrix is dull compared to the infilling cements with foraminifers and other biogenic debris. The matrix is non-ferroan and is identical in fluorescence to the foraminifera shells. In the carbonate-rich lithofaces (4-7), CL reveals cements are zoned, non-ferroan and overall fluoresce brighter compared to the carbonate in the organic-rich lithofacies (1-3). Infilling cements within foraminifera are also zoned, as are cements surrounding biogenic debris (figure 3.1). Zonations are particularly apparent in the equant cements overprinting the original fabric and surrounding biogenic debris. In lithofacies 7, CL shows bright fluorescing, non-ferroan, non-zoned calcite cements which are present throughout the entire assemblage (figure 3.1).
Figure 3.2. Original and diagenetic calcite cements in the Eagle Ford Fmn. Note: All sample locations can be located by well and depth in the appendix. Well locations are shown in Figure 3.0.

A. Sample D1S1-LEF, outcrop sample GPS location 29.3797, -101.2038. Argillaceous mudstone in PPL, containing planktonic foraminifera (F) infilled with early authigenic calcite cement (C). Floating dolomite rhombs (D) are present in the micritic matrix.

B. Sample Shell Hay E-D 13,751.00. A weakly laminated mudstone containing planktonic foraminifera (F) infilled with early authigenic calcite cement.

C. Sample Orts 7678.5. Laminated Foraminiferal-rich Wackestone in PPL, containing planktonic foraminifera (F) infilled with early authigenic calcite cement (C). Cements (C) have also precipitated around the cements, attaching foraminifera together with cement.

D. Sample 38 54.7D. Bioturbated lime mudstone to wackestone in PPL, containing foraminifera infilled with calcite (C) and recrystallised cements (C) overprinting the matrix.

E. Sample H-P Orts, 7691.6 ft of a Foraminifera dominated Packstone to Grainstone. Formaminifera infilled with authigenic calcite dominates the assemblage with little other minerals present. Framboidal pyrite it present on top of calcite cements.

F. SEM, energy-dispersive X-ray spectra of dolomite from the dolomitic rhombs (D) present in the argillaceous mudstones.

G. Sample Leppard 13598.6. SEM-BSE image, displaying benthic foraminifera infilled with calcite (C) and kaolinite (K). In this particular example the foram shell walls (FS) have been recrystallised.

H. Sample Leppard 13582.4. SEM-BSE image displaying planktonic foraminifera infilled with calcite (C), chlorite (Ch), and dolomite (D).

The presence of non-ferroan calcite cements and poly-framboidal pyrite in the Lower Eagle Ford Fmn, strongly suggest microbially-mediated sulphate reduction caused the sequestration of iron and sulphide into pyrite. Due to the location of calcite cements within foraminifera chambers, the overall volume and texture together with the preservation of uncompacted foraminifera shells, indicates cements were precipitated prior to significant compaction throughout the Eagle Ford Fmn (Irwin, 1977, Scotchman, 1989, Al Balushi et al., 2013, Taylor and Macquaker, 2014). The lack of burrowing (Figure 3.1) in lithofacies 1, 2 and 3, high TOC values and the presence of pyrite suggests sulphate reduction was the main driver of reduction in these sediments during deposition, with little to no oxygen present to support faunal communities living on the sediment water interface.

Recrystallisation of carbonate is a common diagenetic feature throughout the Eagle Ford Fmn and is observed at many scales and in various quantities. Under SEM recrystallisation has occurred in the organic-rich lithofacies (1, 2 and 3) at a smaller scale compared to the carbonate-rich lithofacies. Electron microscopy shows the bulk of carbonate observed in XRD is present as micro-crystalline (2-5µm) euhedral crystal shape calcite grains that are present as a key component of the micritic matrix. These calcite grains are observed as midly recrystallised coccolith debris.
Like the organic-rich lithofacies (1-3), the carbonate rich-lithofacies (5-7), also contain non-ferroan calcite cements and poly-framboidal pyrite. However these cements are commonly zoned when observed in CL. The volume of calcite cement has increased and the location of these cements extends to overprinting the original assemblage, with ranges of 60-90% content depending on the lithofacies (Table 3.1). With the presence of benthic foraminifera and a diverse assemblage of reworked skeletal debris (lithofacies 5), burrows, and low TOC values, an oxygenated depositional environment is inferred. Burrowing present in lithofacies 5 and 6 indicates stable, well oxygenated marine conditions where faunal communities can accumulate within the sediment water interface (Al Balushi et al., 2013, Corbett and Watkins, 2013, Lowery et al., 2014, Pederson and Calvert, 1990). Infilled and preserved foraminifera, suggest non-ferroan, zoned calcite cements and poly-framboidal pyrite were precipitated early, prior to compaction. Additionally with low TOC values we infer aerobic oxidation of organic matter occurred in these lithofacies (Reaction 3). Especially in lithofacies 6 and 7, where calcite content is 78 and 90% respectively, and TOC values are <0.5% (table 3.1).

Bulk $\delta^{13}$C stable isotopes (figure 3.0), show the carbonate (coccolith debris) within the organic-rich lithofacies have an average $\delta^{13}$C composition of 0.62‰ VPDB (figure 3.0). Average bulk $\delta^{18}$O stable isotopes for the organic-rich lithofacies is $\delta^{18}$O -6.86‰ VPDB (figure 3.0). Bulk $\delta^{13}$C values (~ 0 to 1‰ VPDB) (figure 3.0) suggest carbonate is mainly derived from a marine source and not microbial processes, suggesting carbonate was precipitated at, or very close to the sediment water interface (Irwin, 1977, Berner and Faber, 1996, Arthur and Anderson, 1983, Anderson and Arthur, 1983).

Recrystallisation is also observed in optical microscopy in the carbonate-rich lithofacies (figure 3.1 and 3.2). It is particularly prominent in lithofacies 6, with a significant quantity of micro-cement grains overprinting the original composition. However, a vast quantity of foraminifera shells remain, with recrystallised cements surrounding and infilling them (figure 3.2). The carbonate-rich lithofacies (5-7) have an average bulk stable $\delta^{13}$C composition of -1.91‰ VPDB and average $\delta^{18}$O isotopic compositions of -5.02‰ VPDB (figure 3.0). Textures which suggest recrystallisation were not observed under SEM or optical microscopy in the foraminiferal dominated packstone to grainstones (lithofacies 7). Cements in this facies look to be
precipitated in one phase. The bright fluorescing cements observed in lithofacies 7, with high pyrite content are also indicative of sulphate reduction. However zonations of the calcite cements are absent suggesting pore water chemistry was relatively stable compared to lithofacies 5 and 6 during carbonate precipitation and the carbonate was precipitated rapidly in one phase (Macquaker et al., 1997, Taylor and Macquaker, 2014, Curtis, 1977, Curtis and Spears, 1968, Al Balushi et al., 2013, Azmy et al., 2008).

Figure 3.2. Calcite in catholuminescence (CL). **Note:** All sample locations can be located by well and depth in the appendix. Well locations are shown in Figure 3.0. A. Thin section of Shell Hay E-D 13,751.00 - a weakly laminated mudstone containing planktonic foraminifera (F) infilled with early authigenic calcite cement. Some cements within the foraminifers contain zonation’s, indicating pore water chemistry variations during deposition. Shell walls remain black, indicating they are the original shell material and have not been recrystallised. The remix remains dull compared to the authigenic cements inside foraminfera chambers, suggesting the carbonate here is marine derived (detrital) derived. B. Sample D1S1-LEF, outcrop sample GPS location 29.3797, -101.2038. Argillaceous mudstone in PPL, containing planktonic foraminifera (F) infilled with early authigenic calcite cement (C). Shell walls remain black, indicating they are the original shell material and have
not been recrystallised. The matrix also remains dull compared to the authigenic cements inside foraminifera chambers, suggesting the carbonate here is marine derived (detrital) derived. **C. Sample H-P Orts, 7691.6 ft of a Foraminifera dominated Packstone to Grainstone.** Formaminifera infilled with authigenic calcite. Bright, non-ferroan, non-zoned calcite cement. A lack of zonations, early cementation with consistent pore water chemistry suggests aerobic oxidation of organic matter precipitating calcite. **D. Sample 38 54.7D. Bioturbated lime mudstone to wackestone in CL, containing foraminifera infilled with calcite and recystallised cements (FC) overprinting the matrix.** Foraminifers contain zonation’s, indicating pore water chemistry variations during deposition. Shell walls remain black, indicating they are the original shell material and have not been recrystallised.

In thin section the argillaceous mudstones contain floating silt sized particles that were originally thought to be crushed foraminifera chambers or radiolarian shells. Further analysis under SEM revealed the floating silt sized particles were in fact calcitic dolomite rhombs (figure 3.1). Dolomite makes up a very small percentage of the total rock composition (<1%) in the Eagle Ford Fmn and is only present in the argillaceous mudstones (1), the weakly laminated mudstones (2) and foraminiferal dominated packstone to grainstones (7). There is no siderite or ankerite observed in thin section or in XRD.

Pyrite is a common mineral observed in both the Lower and Upper Eagle Ford Fmn. Pyrite is present in all lithofacies, although its abundance varies. In the Lower Eagle Ford Fmn pyrite is observed under SEM as framboids on post-dating calcite and kaolinite cements (Figure 3.2). A small proportion is observed as larger (~50µm) euhedral fragments present within the matrix, which can be observed under optical microscopy as black nodules (Figure 3.2). In the carbonate-rich lithofacies pyrite is observed as ~50 µm euhedral fragments within the matrix sitting on top of calcite cements and infilling biogenic debris (figure 3.2).

Pyrite is more abundant in the argillaceous mudstones (Figure 3.1) compared to the other organic-rich lithofacies (weakly laminated mudstones and laminated foraminifera-rich wackestones) (Table 3.1). Pyrite abundances are less in the skeletal wackestone to packstones, bioturbated lime mudstones to wackestones and foraminiferal dominated packstones to grainstones, which contain smaller quantities of pyrite (Figure 3.1). The recrystallised lime wackestones contain negligible abundances of pyrite. The presence of non-ferroan calcite cements and poly-
framboidal pyrite in the Lower Eagle Ford Fmn, strongly suggest microbially-mediated sulphate reduction caused the sequestration of iron and sulphide into pyrite.

Figure 3.3. Pyrite and gypsum in thin section, SEM and outcrop of the Eagle Ford Fmn. Note: All sample locations can be located by well and depth in the appendix. Well locations are shown in Figure 3.0. A. Sample Hurt Lloyd 7215.0. Foraminiferal dominated packstone to grainstone in PPL, containing benthic foraminifera (F) infilled and overprinted with early authigenic calcite cement (C) and pyrite (Py). Pyrite (black circular nodules) framboids are distinctive in the carbonate rich facies due to the contrast in colour. B. Sample 7236.8. Bioturbated lime mudstone to wackestone in PPL.
containing infilled foraminifera (F) and pyrite (Py). Pyrite (black circular nodules) is present within foramin chambers and the micritic matrix. C. Sample Hay 13643.7. SEM BSE image of a weakly laminated mudstone containing pyrite framboïds (Py), calcite (C) and organic matter (OM) infilled foraminifera. D. Sample 2779990. SEM BSE image of a bioturbated lime mudstone to wackestone displaying a diatom (recrystallised) infilled with kaolinite (K) and pyrite (Py). E. Outcrop photo displaying gypsum (G) veins present in the lower organic rich Eagle Ford (pencil for scale) GPS location 29.3793, -1012038. F. Outcrop photo displaying a close up of a gypsum vein in the lower organic rich Eagle Ford (pencil for scale). GPS location 29.3793, -1012038

3.3.2 Gypsum

Gypsum comprises a very small total of the overall rock volume in the Eagle Ford Fmn (<1%). Gypsum is observed as veins in the outcrops of the organic-rich, Lower Eagle Ford Fmn (figure 3.2). Gypsum veins are rarely observed in the outcrops of the Upper Eagle Ford Fmn. Gypsum veins are not present in core throughout the formation. XRD results from core samples reveal negligible gypsum content in lithofacies 1 and 2 (0.5%), but is present in substantial quantity from outcrop samples and is clearly visible in situ (figure 3.2).

3.3.3 Kaolinite

Kaolinite is observed throughout the Eagle Ford Fmn and is present in all lithofacies. Kaolinite is observed in three main forms. 1) Under SEM, as micro-sized crystals within the matrix. 2) Large booky cements that look to have replaced silt sized detrital feldspars. 3) Booky cements that have infilled foraminifera (Figure 3.6). The latter is commonly observed in optical microscopy as a brown, grainy texture inside foraminifer’s chambers. The infilling of foraminifera with kaolinite is common in organic-rich lithofacies 2 and 3. The laminated foraminiferal-rich wackestones (3) contain the most foraminifera infilled with kaolinite with the bulk of kaolinite observed within foraminifera. XRD shows the argillaceous mudstones (1) contain 5% kaolinite, however over 85% of the kaolinite is observed as micron-sized crystals within the matrix (Figure 3.6). The remaining 15% is present within foraminifers’ chambers. In the weakly laminated mudstones there is an equal distribution of kaolinite observed between infilling foraminifers’ and micro-size cements in the matrix (Figure 3.6). Foraminifers’ chambers that are clay infilled do not contain mixed layer I/S, only kaolinite or chlorite. In the carbonate rich lithofacies; skeletal wackestone to packstone and bioturbated lime mudstone to wackestones there is an
overall decrease in kaolinite content, 3-4% (table 3.1). Over 70% of the kaolinite in these facies is seen as micro-sized crystals within the matrix. The remaining 30% is seen as replacing silt sized detrital feldspars or infilling foraminifers, although the latter is rare (figure 3.6). Kaolinite is rarely observed in the foraminiferal dominated packstone to grainstones. XRD shows kaolinite content is 0.5% in this lithofacies (table 3.1). Overall, kaolinite is most abundant in the Lower Eagle Ford Fmn (Table 3.1 and Figure 3.4), where lithofacies 1 and 2 are most prevalent. None of the Eagle Ford Fmn samples contain apatite, although in some lithofacies, in particular the skeletal wackestone to packstones, fish debris are commonly observed.

3.3.4 Mixed layer Illite/Smectite

Mixed layer illite/smectite (I/S) is the most abundant clay mineral in the Eagle Ford Fmn table 3.1 and figure 3.4). Illite is the second most abundant (Table 3.1 and Figure 3.4). Mixed layer I/S and illite is present throughout the Eagle Ford Fmn. The two clay minerals are more abundant in the Lower Eagle Ford Fmn due to the overall increased clay content. The ratio (3:2) of mixed layer I/S to illite stays fairly constant throughout the Eagle Ford Fmn (figure 3.3). Burial diagenesis overall increases the ratio of illite to mixed layer I/S (figure 3.3). Smectite, is not present in the Eagle Ford Fmn, suggesting all smectite has been converted to mixed layer I/S during diagenesis. Smectite is present in samples obtained from outcrops, suggesting the outcrops were not buried deep enough, or long enough, or both, for all smectite to transform into mixed layer (I/S).

Under SEM, lithofaices 1-3 contain abundant mixed layer (I/S) and illite which are identifiable as 2-4µm sized wisps interspersed between coccolith fragments and organic material in the micritic matrix (figure 3.4). Both clay minerals are confined to the matrix and do not appear within biogenic material, such as foraminifera chambers or diatoms. They commonly have carbonate and silicate cements proceeding them (figure 3.4). In the carbonate-rich lithofacies, mixed layer I/S and illite are present but in much smaller quantities due to an overall reduction in clay content and increase in carbonate content (figure 3.3). Lithofacies does not seem to affect the ratio of mixed layer I/S to illite ratio (figure 3.3). However the ratio of
mixed layer I/S to kaolinite and chlorite does vary throughout the Eagle Ford Fmn (Figure 3.4).

Figure 3.4. XRD analysis (clay fraction only), of the Statoil/Talisman core displaying the clay mineral distribution throughout the Eagle Ford Fmn. Depths, length and overall stratigraphy are unknown. Note, the absence of smectite due to the full conversion to mixed layer illite/smectite. Authigenic kaolinite and chlorite is only present in the Lower and Mid Eagle Ford, with negligible kaolinite present in the Upper section. Kaolinite present in the Upper Eagle Ford is only observed infilling foraminifera, though rare. Source, Statoil ASA. The Middle Eagle Ford Fmn is an interpreted transition zone where Lower Eagle Ford transitions into the Upper Eagle Ford Fmn.
3.3.5 Quartz

Quartz is a common mineral observed throughout the Eagle Ford Fmn (table 3.1 and figure 3.4). The Lower Eagle Ford Fmn is abundant with quartz with average values of ~19% across the three organic-rich lithofacies (table 3.1). Quartz content in the Upper Eagle Ford Fmn varies between 4-7%. The highest quartz content is seen within the argillaceous mudstones at 22%. The other organic rich lithofacies and the skeletal wackestones to packstones (2, 3 and 5) contain considerably less quartz, 18, 15 and 7% respectively. The remaining lithofacies rich in carbonate have a range of quartz content from 4-7%.

Quartz is seen under SEM in three main forms: 1) Equant cements varying in size from 3-10µm in diameter, precipitated next to or on top of calcite cements or foraminifera shells. 2) Large, angular silt sized (>62.5μm) grains within the matrix. 3) Seen as micro-cements (1-3µm), infilling porosity between coccolith fragments within the matrix (figure 3.4). Despite no SEM- CL analysis undertaken in this study, the large angular silt sized quartz grains are thought to be detrital quartz grains and are rarely observed throughout the lithofacies and entire Eagle Ford Fmn. Forms 1 and 3 are interpreted to be authigenic quartz due to their volume, texture and location. The precipitation of authigenic quartz is a late diagenetic process due to the high temperatures needed to precipitate quartz (Thyberg and Jahren, 2011).

In the argillaceous mudstones (lithofacies 1), 3-10µm equant cements present on top of clay minerals are almost exclusively the only form of quartz cements observed. Micro-cements are also present but constitute <5% of overall quartz content. Detrital quartz grains were observed too in this lithofacies, but constitute a small (<1%) amount of the total quartz volume. In lithofacies 2 and 3, micro-cements which vary between 1-3 µm in size, constitute 80% of the quartz content, which has precipitated between and on top of coccolith fragments and mixed layer I/S and illite grains. Equant cements make up the remaining 20% of the total quartz volume and are found on top of calcite cements, coccolith fragments and other biogenic material (figure 3.3). In the carbonate-rich lithofacies, the vast majority of quartz is seen as 3-10 µm equant cements next to or on top of calcite cements within the micritic matrix. The rest is 1-3 µm micro-cements also within the micritic matrix (figure 3.3). Detrital quartz is rarely observed in these lithofacies.
Figure 3.5. Quartz and mixed layer illite/smectite present in the Eagle Ford Fmn. Note: All sample locations can be located by well and depth in the appendix. Well locations are shown in Figure 3.0.

A. Sample Hurt Lloyd 7285.0. SEM-BSE image. Authigenic equant quartz (Q) cements precipitated between calcite cements (C) in a bioturbated lime mudstone to wackestone. B. SEM-energy dispersive X-ray spectra, showing the chemistry of quartz under SEM (darker coloured grains). C. SEM-energy dispersive X-ray spectra. A characteristic EDS spectrum of the chemistry of mixed layer I/S in the micritic matrix. D. Sample Shell J-A Leppard 1-H 13665.3, SEM-BSE image at high magnification displaying mixed layer I/S between coccolith fragments (CC) in the micritic matrix. Authigenic equant and micro quartz cements have proceeded the I/S and coccolith fragments. E. Sample Leppard 13665.3. SEM-BSE image. Authigenic equant quartz (Q) cements, mixed layer I/S and kaolinite (K) replacing K-feldspars within an argillaceous mudstone. F. Sample Mathews 4673.00. 4-5μm authigenic micro-quartz cements (Q) overprinting the micritic matrix. Between authigenic quartz grains and coccolith fragments are illite and mixed later I/S grains. G. Sample Matthews #101. A detrital quartz (DQ) grain within a weakly laminated mudstone (centre of image). Detrital quartz grains are interpreted due to their roundness and size.

3.3.6 Chlorite

Chlorite is the last inorganic mineral to be precipitated within the Eagle Ford Fmn. Like the previous clay minerals (mixed layer I/S, illite and kaolinite), chlorite is most abundant (2.5%) in the argillaceous mudstones (1) and, overall in the Lower Eagle Ford Fmn (table 3.1 and figure 3.5). Chlorite is also present in the weakly laminated mudstones (2) but in smaller quantities (~1.1%) (table 3.1). Unlike kaolinite, chlorite is not present in the upper Eagle Ford and is only present in the two most clay-rich lithofacies (1 & 2), where there is abundant mixed layer (I/S) and kaolinite. Chlorite is observed to have precipitated as two main forms within the Eagle Ford Fmn, both of which are Fe-rich (figure 3.5). 1) 70% of chlorite is seen within foraminifera chambers. 2) The remaining 30% of chlorite is observed intergrown within I/S and coccolith fragments in the matrix (figure 3.5). Samples that contain chlorite have a depleted kaolinite content compared to samples with a similar total clay volume but no chlorite is present. This is seen between the average clay composition differences between the argillaceous mudstones and weakly laminated mudstones (table 3.1).

Kaolinite and chlorite grains display deformation under SEM, with grains commonly squashed and folded; a sign that overpressure is present in the sub-surface. The
expulsion of water from clay mineral reactions and hydrocarbons due to maturation and generation can result in overpressure.
Figure 3.6. Authigenic kaolinite and chlorite in the Eagle Ford Fmn. **Note:** All sample locations can be located by well and depth in the appendix. Well locations are shown in Figure 3.0. A. Sample Hurt Lloyd 7219.60. Thin section micrograph in PPL displaying a laminated foraminifera rich wackestone containing infilled foraminifera with kaolinite (K). Note the vast majority of forams are infilled with calcite. B. Sample Hay 13820.9. SEM-BSE image of an argillaceous mudstone. Kaolinite (K) infills a planktonic foraminifera test (F), indicating kaolinite was likely to be an early diagenetic process. Diatoms (Di) are common and are often infilled with bitumen and organic matter. C. Sample Leppard 13665.0. SEM-BSE image of a foraminifera test (F), infilled with organic matter, calcite cements (C), and kaolinite books (K). An authigenic quartz grain (Q) has precipitated next to the foram test on top of coccolith fragments and mixed layer I/S. D. Sample 229971. SEM-BSE image of a detrital k-feldspar grain (orthoclase), replaced with kaolinite (K). Note; the high abundance of angular calcite grains in the matrix (coccolith fragments). E. Sample 227991. SEM-BSE image of a foraminifera test (F) infilled with bitumen (OM). Chlorite (Ch) has precipitated out of phase into the matrix between quartz and calcite cements. F. SEM, energy-dispersive X-ray spectra of chlorite. Chlorite is similar to kaolinite with high Al and Si peak, however chlorite also contains a distinct Fe or Mg peak. Chlorite in the Eagle Ford Fmn contains Fe. G. Sample 2779978. SEM-BSE image at high magnification of kaolinite (K) and chlorite (Ch) within the matrix. Both are interpreted to have precipitated out of fluid phase in this particular image, with chlorite proceeding kaolinite. H. Sample Matthews 4773.50. SEM-BSE image at high magnification of a foraminifera test composed of calcite (C). Part of the infilling calcite cement has been dolomitised (D). Kaolinite books (K) infill the outer part of the foram chamber with the centre books pseudomorphed into chlorite (Ch).

The Lower Eagle Ford Fmn contains a significant amount of organic carbon (3.8-6.2 wt% TOC). Bitumen infilling shelter and intra-particle porosity (mainly within biogenic debris), and micro-porosity between coccolith fragments and clay minerals is commonly observed under SEM (figure 3.2, 3.5). Bitumen is observed in the Upper Eagle Ford Fmn, but is observed mainly infilling intra-crystalline porosity within quartz and carbonate cements (Figure 3.5) and kaolinite cements (figure 3.6). The presence of bitumen within biogenic debris indicates the formation has been buried to sufficient depth where organic matter maturation, generation and expulsion of hydrocarbons have been able to occur.
3.3.7 Paragenetic History

The timing, and prevalence of each diagenetic process which has taken place in the Eagle Ford Fmn is best visualised in the paragenetic sequence charts below (Figures 3.7 and 3.8). The charts are based on lithofacies identified in the formation (see Table 3.1), with the clay and organic-rich facies (1, 2 and 3) placed in first chart. The first three lithofacies contain a similar paragenetic history, with negligible variation between processes. Outright additional or absence of particular diagenetic processes between the organic-rich lithofacies (1-3) are: 1) The precipitation of dolomitic rhombs within the matrix of the argillaceous mudstones and weakly laminated mudstones (lithofacies 1). 2) The absence of dolomitisation of foraminifera shell walls in the laminated foraminiferal-rich wackestones. 3) The absence of chlorite in the laminated foraminiferal rich wackestones (Figure 3.7). Bar these key additions or absences in diagenetic products, the differences between the three lithofacies are the volume of particular minerals precipitated in each lithofacies.
Sulphate reduction is interpreted to be one of the first diagenetic reactions to take place in the organic-rich, TOC-rich lithofacies (Figure 3.7 and 3.2). The presence of non-ferroan calcite cements and poly-framboidal pyrite in the Lower Eagle Ford Fmn, strongly suggest microbially-mediated sulphate reduction caused the sequestration of iron and sulphide into pyrite. Sulphate reduction is also the likely cause of non-ferroan calcite cements. The location of calcite cements within foraminifera chambers, the overall volume and texture together with the preservation of uncompacted foraminifera shells, indicates cements were precipitated prior to significant compaction throughout the Eagle Ford Fmn and therefore were the first
minerals to be precipitated. The degradation of organic matter via microbially mediated sulphate reduction and thermo-chemical decay (catagenesis) during burial are associated with organic acids being produced and entering the pore fluids at depths beyond 10m. These acids are interpreted to dissolve radiolarian shells, while during the same period precipitate authigenic kaolinite within foraminifera chambers (Figure 3.7 and 3.6). The presence of kaolinite cements within uncompacted planktonic and benthic foraminifera chambers in lithofacies 1-3, indicates kaolinite was being precipitated relatively early during burial. This implies dissolved silicate and aluminium was present in the pore fluids during early diagenesis, prior to significant compaction in the Eagle Ford Fmn. This allowed kaolinite to precipitate within foraminifera chambers whilst calcite was precipitating at the same time (Figure 3.1 and 3.6). It is unlikely that kaolinite displaces calcite later in diagenesis; inferring kaolinite was precipitated during early diagenesis. The presence of organic acids in the pore waters is interpreted to cause the precipitation of dolomite in and around foraminifera shells (Figure 3.1 and 3.2). Free Mg ions were likely to be present due to organic-complexing reactions of organic matter and possibly the dissolution of feldspars. Due to the lack of blocky calcite cement in the organic-rich lithofacies (1-3), we infer mild recrystallisation of the coccolith fragments has occurred due to their euhedral like shape under SEM-backscatter images and their $\delta^{18}O$ compositions (Figures 3.0 and 3.1). Despite a later phase of carbonate recycling, this has not altered the $\delta^{13}C$ signatures (figure 3.0). The smectite/illite reaction generally starts to take place in similar burial depths and temperatures to hydrocarbon generation. Here illite sheets replace smectite and release vast quantities of minerals and ions into the surrounding assemblage. During this period of burial, authigenic micro-quartz grains are interpreted to precipitate out of solution as abundant free Si ions are given off from the smectite/illite transition. Authigenic micro-quartz is interpreted to precipitate at considerable depths (>90m) because grains always overly other grains present, except for chlorite (Figure 3.5, 3.6 and 3.7) Chlorite is then the last mineral to be precipitated due to Fe, Mg and Si ions released from the smectite/illite reaction proceeding it.

The carbonate-rich lithofacies (skeletal wackestones to packstones, bioturbated lime mudstones to wackestones, recrystallised foraminiferal dominated packstone to grainstones) are represented in Figure 3.8. These three lithofacies contain similar
paragenetic processes and timings. There are additional and absences of diagenetic processes between the carbonate-rich lithofacies, they are: 1) The early recrystallisation of cements and foraminifers in the bioturbated lime mudstones to wackestones. 2) In the foraminiferal dominated packstone to grainstones dolomitisation occurs during late diagenesis within the cements, although this process is on a very small scale. 3) The replacement of K-feldspars with kaolinite is only observed in the skeletal wackestones to packstones. Due to low TOC values observed in the bioturbated lime mudstone to wackestones and foraminiferal dominated packstone to grainstone we infer negligible quantities of hydrocarbons were generated and expelled from these lithofacies relative to the rest of the lithofacies observed in the Eagle Ford Fmn (figure 3.8).

Lithofacies 4 is not present in the paragenetic charts. This lithofacies is described thoroughly in the next chapter, while the bentonites (lithofacies 8) are not of diagenetic interest in this study.

Due to the low TOC values we infer aerobic oxidation of organic matter has occurred in these lithofacies, creating TOC lean mudstone and carbonate rocks (Figure 3.8). This is process is interpreted to be the very first process to occur and is likely to have occurred in the water column or at the sediment water interface (Figure 3.8). Burrowing present in the skeletal wackestones to packstones and the bioturbated mudstones to wackestones indicates stable, well oxygenated marine conditions where faunal communities can thrive within the sediment at the sediment water interface. Sulphate reduction is interpreted to be the second diagenetic process to take effect in the carbonate-rich, TOC poor, lithofacies (Figure 3.2 and 3.8). The presence of non-ferroan calcite cements and poly-framboidal pyrite in the Upper Eagle Ford Fmn, strongly suggest microbially-mediated sulphate reduction caused the sequestration of iron and sulphide into pyrite. Sulphate reduction is also the likely cause of non-ferroan calcite cements; however the bright fluorescing cements observed in the foraminiferal dominated packstones to grainstones, with high pyrite content are indicative of sulphate reduction (Figure 3.1 and 3.2). However, zonations in calcite cements are absent suggesting pore water chemistry was relatively stable compared to the skeletal wackestones to packstones and the bioturbated mudstones to wackestones during carbonate precipitation and the carbonate was precipitated rapidly in one phase. This suggests oxygen was present in the first 2-3m of sediment
and created more stable conditions (Figure 3.2 and 3.8) The degradation of organic matter via microbially mediated sulphate reduction and thermo-chemical decay is interpreted to have taken place at shallow depths, because kaolinite is present within foraminifera in the carbonate-rich lithofacies in the Upper Eagle Ford Fmn. This process is interpreted to have occurred relatively early as kaolinite infills foram chambers before calcite does (Figure 3.8). It is unlikely that kaolinite displaces calcite later in diagenesis; inferring kaolinite was precipitated during early diagenesis. Large kaolinite grains are interpreted to have replaced feldspars within the Upper Eagle Ford Fmn lithofacies (Figure 3.6). This is interpreted to happen after the bulk of authigeneic kaolinite has precipitated in foraminifera due to the appearance of replaced feldspars in thin section. Large kaolinite grains (20-30µm) appear to sit on top of the matrix and other grains suggesting the process occurred later in burial (Figure 3.6). The presence of organic acids in the pore waters is interpreted to cause the precipitation of dolomite in and around foraminifera shells is due to free Mg ions were likely to be present due to organic-complexing reactions of organic matter and the resulting dissolution of feldspars.. In the foraminiferal dominated packstones to grainstones, dolomitisation is interpreted to occur at a similar time during burial with Al able to replace K and Mg from feldspars. (Figure 3.2 and 3.8). The recrystallisation of coccolith fragments has occurred at depth giving negative δ^{18}O compositions (40-60°C) (Figure 3.0). The temperatures indicated infer this process occurred at significant depth (~100m/330ft) and not at near the surface at much lower tewmperatures. Quartz is interpreted to be precipitated after the precipitation of kaolinite. Free Si ions derived from dissolved radiolarians and other amorphous material containing Si (opal A/CT), is believed to have driven kaolinite authigenesis due to organic acids being present early diagenesis. (Figure 3.8). Any free Si ions were the available for micro and euhedral authigenic quartz cements to precipitate. Additional Si is thought to have been derived from the smectite/illite reaction, although this process is less of a factor in the Upper Eagle Ford Fmn due to the overall lower clay content. Euhedral quartz cements are often observed overlying coccolith fragments and carbonate cement grains, indicating they precipitated later in burial (Figure 3.8).

A key difference between the organic-rich lithofacies (1-3) in the Lower Eagle Ford Fmn and the carbonate rich lithofacies (5-7) in the Upper Eagle Ford Fmn is clay
volume. The organic-rich lithofacies, especially lithofacies 1 and 2, contain significant volumes of clay minerals (44% and 27% respectively) (Table 3.1 and Figure 3.1). The presence of clay minerals is important because they are highly reactive and chemically unstable in pore water systems due to their large surface area and free ion groups available. The presence of clay minerals encourage dissolution and precipitation reactions, such as the precipitation of quartz and other clay minerals (kaolinite, chlorite), while the dissolution of carbonate is common place due to the acidic conditions created by clay mineral transformations (Barcelona, 1980, Boles and Franks, 1979, Peltonen et al., 2009). The lower clay content in the Upper Eagle Ford Fmn and higher input of biogenic carbonate allows extensive carbonate precipitation in and around biogenic debris, such as in foraminifera and primary porosity. Another key difference is vast evidence of oxygen present in the water column and/or at the sediment water interface during deposition of the Upper Eagle Ford Fmn. Extensive burrowing in the skeletal wackesontes to packstones and bioturbated lime mudstones to wackestones suggests and lower TOC values compared to the lithofacies present in the Lower Eagle Ford Fmn, suggest the presence of oxygen has degraded organic matter before it has been buried. This has created the organic-poor lithofacies in the Upper Eagle Ford Fmn compared to the organic-rich lithofacies in the Lower Eagle Ford Fmn.

Due to the lower TOC content in the Upper Eagle Ford Fmn, hydrocarbon expulsion is much less compared to the Lower Eagle Ford Fmn. The skeletal wackestones to packstones are the only lithofacies in the Upper Eagle Ford Fmn that can contain significant organic content and therefore, expel hydrocarbons. The bioturbated lime mudstones to wackestones and foraminiferal dominated packstones to grainstones are interpreted not to expel any hydrocarbons at all due to their low TOC content (~0.5%, see Table 3.1) and very high carbonate content (>90% see Table 3.1 and Figure 3.1). Carbonate cement content over 90% is likely to close any porosity in these lithofacies. If there are pockets of significant organic content capable of generating hydrocarbons, it is unlikely they would able to flow due to the low porosity closed up by carbonate cements.
Figure 3.8. Paragenetic sequence chart reconstructed for the; 5. Skeletal Wackestone to Packstones (dark blue bars). 6. Bioturbated Lime Mudstone to Wackestones (light blue bars). 7. Recrystallised Foraminiferal dominated Packstone to Grainstone (bright blue bars). The three lithofacies are carbonate-rich and organic matter poor, and contain similar paragenetic histories. Lithofacies 7 has an abundance of calcite interpreted to have precipitated due to the oxidation/degradation of organic matter, hence the longer bright blue bar. O$_2$ denotes aerobic oxidation of organic matter. SR denotes sulphate reduction. All reactions are interpreted to have occurred at a similar time relative to depth of burial.
3.4 Interpretation and Discussion

Detailed observations of thin sections using optical and electron-optical methods, along with inorganic and organic geochemistry can significantly increase our understanding and knowledge of diagenetic pathways in fine grained mudstones. The results from our study show the complex interplay of different factors which control composition and heterogeneity in the Eagle Ford Fmn. Diagenesis has a significant role on mudstone composition, with this itself influenced by a variety of factors. The main factors are: eustatic sea level variation (most likely fifth order scale fluctuations but with an overall transgression during the Late Cretaceous during Eagle Ford Fmn deposition), primary production, sedimentation rates, sea water geochemistry and bottom water current activity (Bohacs, 1990, Bohacs, 1998, Worden et al., 2000a, Worden et al., 2000b, Schmalz, 1967, Brigaud et al., 2009, Al Balushi et al., 2013).

Diagenetic reactions however, are interpreted to be the main driver of mineralogical and geochemical composition, and therefore lithofacies variation observed the Eagle Ford Fmn. Previous authors have concluded that early diagenetic reactions in marine derived mudstones are often the processes that have the biggest influence on the composition of a source rock/mudstone (Claypool, 1974, Curtis, 1977, Irwin, 1977, Coleman, 1985, Taylor, 2010, Macquaker et al., 2014). Diagenetic processes occurred very early in the Eagle Ford Fmn- probably immediately after deposition and arguably during deposition in the case of the Upper Eagle Ford Fmn as sediment and organic matter fell in transit through the water column. Early diagenetic processes are mostly bacterially driven (Curtis, 1977, Friedman, 1964, Michalopoulos and Aller, 2004, Reinhard, 1986, Yamaguchi et al., 2010). The diagenetic processes interpreted to have taken place during burial of the Eagle Ford Fmn due to the presence of equant calcite cements and poly-framboidal pyrite (figures 3.1, 3.2, 3.6 and 3.7).

Early diagenetic reactions are controlled by the availability of reductants (organic matter) and oxidants (oxygen, iron oxides, nitrate, manganese and sulphate (references). If these are bioavailable, they can support a variety of bacterial metabolic pathways that may precipitate mineral cements within uncompacted mudstones (Friedman, 1964, Reinhard, 1986, Curtis, 1977, Curtis, 1995). Mudstones deposited on continental shelves in relatively shallow seas are dominated by aerobic
and anaerobic oxidation through iron (Reaction 1), and sulphate reduction (Reaction 2), (Aller and Blair, 2006, Aller et al., 2004, Macquaker et al., 2014, Taylor and Macquaker, 2014). In anoxic settings anaerobic microbial metabolism (see Chapter 1), causes the pore waters in uncompacted sediments to contain high concentrations of bicarbonate, sulphide and iron (Curtis, 1977, Curtis and Spears, 1968, Macquaker et al., 1997). This leads to a variety of minerals precipitated such as iron sulphides (pyrite) and non-ferroan calcite and dolomite cements. These cements produce an assemblage that is commonly observed in many siliciclastic, and carbonate dominated fine-grained sedimentary successions (Curtis, 1977, Presley and Kaplan, 1968, Macquaker et al., 2014, Taylor and Macquaker, 2011, Taylor and Macquaker, 2014, Taylor et al., 2010). This cement assemblage, as described above, has been observed in units such as the Devonian Chattanooga Shale in the USA (Schieber, 1999), the Upper Cretaceous Mancos Shale in the USA (Macquaker, 2007), the London Clay formation, the Kimmeridge and Oxford Clay’s in the UK, (Macquaker, 2014, Macquaker et al., 1997, Macquaker and Gawthorpe, 1993, Macquaker and Jones, 2002) and now the Eagle Ford Fmn in southwest Texas, USA.

### 3.4.1 Iron and Sulphate Reduction

The presence of non-ferroan calcite cements and poly-framboidal pyrite in the Lower Eagle Ford Fmn, strongly suggests microbially-mediated sulphate reduction caused the sequestration of iron and sulphide into pyrite. (Irwin, 1977, Barcelona, 1980, Schmalz, 1967, Matthews, 1968, Oertel and Curtis, 1972, Curtis and Spears, 1968, Curtis, 1977, Curtis, 1995). Due to the location of calcite cements within foraminifera chambers, the overall volume and texture together with the preservation of uncompacted foraminifera shells, indicates cements were precipitated prior to significant compaction throughout the Eagle Ford Fmn (Irwin, 1977, Scotchman, 1989, Al Balushi et al., 2013, Taylor and Macquaker, 2014). High TOC values and the presence of pyrite suggests sulphate reduction was the main driver of reduction in these sediments during deposition, with little to no oxygen present to support faunal communities living on the sediment water interface. Despite this, \( \text{H}_2\text{S} \) levels during deposition must have been low. There are no reports of “sour hydrocarbons” in the Eagle Ford Fmn. Kerogen is reported as mainly type-II, with some type-III. There is no sulphur-rich type-IIS (Driskell et al., 2012, Robison, 1997, Lock and Peschier, 2006, Donovan et al., 2012, Martin et al., 2011). This suggests \( \text{H}_2\text{S} \) was
able to diffuse into the overlying water column and/or be sequestered into pyrite (Taylor and Macquaker, 2014, Macquaker et al., 2014, Al Balushi et al., 2013, Canfield et al., 1992, Canfield, 1989, Presley and Kaplan, 1968). Pyrite acts as a sulphide sink and locks H₂S into a solid phase, removing the opportunity for hydrocarbon souring (Macquaker and Adams, 2003, Macquaker et al., 1997, Macquaker et al., 2014, Taylor and Macquaker, 2014, Reinhard, 1986). The implications of a depleted type-IIS source rock, is lower maturity and higher generation temperature of hydrocarbons nearer 80-100°C (Robison, 1997, Pepper and Corvit, 1995). However this is also the reason why the Eagle Ford Fmn produces and expels great volumes of hydrocarbons and is classed as a prolific source rock (Robison, 1997, Pepper and Corvit, 1995). An abundance of pyrite throughout the Eagle Ford Fmn (3-12%), suggests high concentrations of iron were available, allowing for sulphides to be sequestered into a metallic sink instead of organic matter. Bacterially mediated sulphate reduction requires organic material, sulphate and bioavailable oxidised iron (Irwin, 1977, Curtis and Spears, 1968, Curtis, 1977, Macquaker et al., 1997). Various authors have discussed which of the three components are the most important for bacterially mediated sulphate reduction (Canfield et al., 1992, Macquaker et al., 1997, Canfield, 1989, Curtis, 1977). Canfield et al. 1992, discuss how abundance variability of bioavailable sulphate and organic matter, rarely influences pyrite precipitation. Iron oxides however, are the key component. In marine environments, iron input can be restricted, with some environments, particularly distal environments, starved of iron oxide input. An examples of such an environment is the Upper Miocene Monterey Fmn in California, where small quantities of pyrite and low concentrations of iron are found (Curtis and Spears, 1968, Macquaker et al., 1997, Macquaker et al., 2014, Canfield, 1989, Canfield et al., 1992). Iron poor mudstones are common in distal environments where enough fine grained sediment is able to accumulate at the sediment water interface. Downdip of shelf environments and other potential sediment traps, such as ridges (Eagle Ford Fmn - Edwards and Sligo shelves), and environments where the terrestrial supply is iron poor itself are all causes of iron-poor mudstones (Curtis, 1977, Curtis and Spears, 1968, Macquaker et al., 1997, Macquaker et al., 2014, Taylor and Macquaker, 2011). We infer that along with bacterially induced sulphate reduction, iron reduction also took place in the sediment immediately below the seafloor. The presence of non-ferroan carbonates observed in the Eagle Ford Fmn
along with iron disulphides suggests both reactions were taking place at the same time. Reaction 1; simplified bacterially mediated iron reduction:

\[(\text{FeR}) \quad 2\text{Fe}_2\text{O}_3 + \text{CH}_2\text{O} + 3\text{H}_2\text{O} = 4\text{Fe}^{2+} + \text{HCO}_3^- + 7\text{OH}^- \quad \text{(Reaction 1)}\]

and reaction 2; simplified bacterially mediated sulphate reduction:

\[(\text{SR}) \quad 2\text{CH}_2\text{O} + \text{SO}_4^{2-} = \text{HS}^- + \text{H}^+ + 2\text{HCO}_3^- \quad \text{(Reaction 2)}\]

Like the organic-rich lithofacies (1-3), the carbonate rich-lithofacies (5-7), also contain non-ferroan calcite cements and poly-framboidal pyrite. However these cements are commonly zoned when observed in CL. The volume of calcite cement has increased and the location of these cements extends to overprinting the original assemblage, with ranges of 60-90% content depending on the lithofacies (Table 3.1). With the presence of benthic foraminifera and a diverse assemblage of reworked skeletal debris (lithofacies 5), burrows, and low TOC values, an oxygenated depositional environment is inferred. Burrowing present in lithofacies 5 and 6 indicates stable, well oxygenated marine conditions where faunal communities can accumulate within the sediment water interface (Al Balushi et al., 2013, Corbett and Watkins, 2013, Lowery et al., 2014, Pederson and Calvert, 1990). Infilled and preserved foraminifera, suggest non-ferroan, zoned calcite cements and poly-framboidal pyrite were precipitated early, prior to compaction. Additionally with low TOC values we infer aerobic oxidation of organic matter occurred in these lithofacies (Reaction 3). Especially in lithofacies 6 and 7, where calcite content is 78 and 90% respectively, and TOC values are <0.5% (table 3.1). Reaction 3; simplified organic matter oxidation reaction:

\[\text{OM oxidation, CH}_2\text{O} + \text{O}_2 = \text{H}^+ + \text{HCO}_3^- \quad \text{(Reaction 3)}\]

The presence of zoned invasive cements infilling and surrounding biogenic debris which proceed poly-framboidal pyrite, suggests iron reduction and sulphate reduction was prevalent producing calcite cements, while pyrite still acting as a metallic sink for sulphides to be sequestered, instead of the precipitated carbonate (Curtis, 1977, Curtis and Spears, 1968, Macquaker et al., 1997, Macquaker et al.,
2014, Denne et al., 2014). Zonations where cement growths become increasingly dull imply increasing ferrous iron concentrations within the pore waters system as this is represented in the precipitated carbonate. This process reflects the burial of sediments deeper into the sub-surface where they leave the realms of sulphate reduction where ferrous iron can sequestered into carbonate cements (Taylor and Macquaker, 2011, Taylor and Macquaker, 2014, Macquaker et al., 2014, Al Balushi et al., 2013). This is interpreted to be a common process in in lithofacies 5 and 6.

3.4.2 Luminescence and Isotopic Compositions

Fine grained calcite grains (20-40µm) throughout the entire assemblage and their crystalline texture within lithofacies 6 suggest recrystallisation has occurred (Dunham, 1962, Tucker and Wright, 1990, Taylor, 2010, Scholle and Ulmer-Scholle, 2003, Schmalz, 1967). It is difficult to determine when recrystallisation occurred in lithofacies 6. Brighter fluorescing zoned cements and a decrease in pyrite content can suggest a decrease in iron input into the system with carbonate still precipitated via microbially-mediated sulphate reduction (Presley and Kaplan, 1968, Taylor and Macquaker, 2011, Macquaker et al., 1997). However bulk δ¹³C values (~ 0 to 1‰ VPDB) (Figure 3.0) suggest carbonate is mainly derived from a marine source and not microbial processes, suggesting carbonate was precipitated at, or very close to the sediment water interface (Irwin, 1977, Berner and Faber, 1996, Arthur and Anderson, 1983, Anderson and Arthur, 1983). The bright fluorescing cements observed in lithofacies 7, with high pyrite content are also indicative of sulphate reduction. However zonations of the calcite cements are absent suggesting pore water chemistry was relatively stable compared to lithofacies 5 and 6 during carbonate precipitation and the carbonate was precipitated rapidly in one phase (Macquaker et al., 1997, Taylor and Macquaker, 2014, Curtis, 1977, Curtis and Spears, 1968, Al Balushi et al., 2013, Azmy et al., 2008).

Aerobic oxidation of organic matter is a common process in oxygenated marine environments, which produce organic lean, fine-grained mudstones, such as the Upper Eagle Ford Fmn (Pepper and Corvit, 1995, Tyson, 2005, Pederson and Calvert, 1990). The debate whether primary productivity or preservation is the main factor in organic carbon deposition is still debated (Tyson, 2005, Pederson and
Calvert, 1990). In the Western Interior Seaway (WIS) during the Late Cretaceous, it is thought productivity in the surface waters increased during the Turonian compared to the Cenomanian due to volcanic activity providing extra nutrients to the surface waters (Corbett and Watkins, 2013, Donovan et al., 2012, Lowery et al., 2014, Elder, 1988). However transgression allowed fresh deep-boreal water to enter the depositional system from the north, increasing ocean circulation and turnover bringing further nutrients to the surface, but also supplying oxygen to the water column and sediment-water interface (Lowery et al., 2014, Donovan et al., 2012, Corbett and Watkins, 2013, Elder and Kirkland, 1994, Kennedy et al., 2005). Skeletal debris, burrowing and the presence of benthic foraminifers are indicative of oxygen being present at the sediment-water interface for faunal communities to inhabit during the Cenomanian to Turonian transition and the Turonian (Corbett and Watkins, 2013, Lowery et al., 2014). The Upper Eagle Ford Fmn, which is comprised mainly of lithofacies 5-7 (with thin intervals of lithofacies 3), is organic-poor, bioturbated, carbonate dominated and full of benthic foraminifera and other biogenic debris suggesting a fully oxygenated environment (Donovan et al., 2012, Al Balushi et al., 2013, Macquaker and Adams, 2003, Taylor and Macquaker, 2014, Pederson and Calvert, 1990, Tyson, 2005, Ghadeer and Macquaker, 2011).

Paleo-temperatures of pore waters where carbonate was precipitated can be interpreted through bulk stable C and O isotopes (Figure 3.0) (Anderson and Arthur, 1983, Arthur and Anderson, 1983, Berner and Faber, 1996). C and O isotopic compositions can help interpret the overall depositional environment of a mudstone (Irwin, 1977, Al Balushi et al., 2013, Astin and Scotchman, 1988, Scotchman, 1991, Scotchman, 1989, Scotchman et al., 2000). $\delta^{13}$C values of ~0 to 1‰ VPDB reflect carbonate derived from marine waters. Lighter $\delta^{13}$C values (~0 to -2‰ VPDB) suggest carbonate has been produced through diagenetic processes, such as organogenesis through iron and sulphate reduction (Irwin, 1977, Scotchman, 1989, Scotchman et al., 2000). Carbonate with $\delta^{13}$C values of -2 to -10‰ VPDB, suggests diagenetic reactions such as iron and sulphate reduction, and aerobic oxidation of organic matter have taken place, creating heavily degraded organic matter (Irwin, 1977, Scotchman, 1989, Scotchman et al., 2000). Despite the overriding marine signature recorded isotopically in the organic rich lithofacies (1-3) (figure 3.0), infilling, bright, non-ferroan, non-zoned cements infilling planktonic foraminifera
suggest early diagenetic processes taking place in anoxic conditions (Al Balushi et al., 2013, Irwin, 1977, Macquaker et al., 2014, Scotchman et al., 2000). The overriding marine signature is interpreted to be caused by coccolith fragments present in the micritic matrix, which constitute the bulk of carbonate in the organic-rich lithofacies. In lithofacies 5 and 6 of the Eagle Ford Fmn, δ¹³C compositions also indicate a marine derived signature. With a high volume of carbonate derived from skeletal debris and other biogenic material present in thin section, a marine signature is expected. However some samples (see figure 3.0) contain δ¹³C values that suggest early diagenetic processes have had an effect carbonate (-1 to -1.5‰ VPDB). Despite being dominated by benthic foraminifera, δ¹³C values obtained from lithofacies 7 indicate early diagenetic processes such as iron and sulphate reduction, and aerobic oxidation of organic matter. (Astin and Scotchman, 1988, Scotchman et al., 2000, Irwin, 1977, Al Balushi et al., 2013).

Pore-water paleo-temperatures can be estimated from δ¹⁸O compositions (Irwin, 1977). There is no evidence from δ¹⁸O values obtained from the Eagle Ford Fmn that there was fresh water input, or reduced salinity of the sea water (Al Balushi et al., 2013, Irwin, 1977, Marshall and Pirrie, 2013, Azmy et al., 2008). δ¹⁸O values of -6.5 to -7‰ VPDB equate to pore fluid temperatures of 50-60°C (Kim and O'Neill, 1997, Anderson and Arthur, 1983). Pore fluids at such temperatures suggest calcite was precipitated at depth (Scotchman et al., 2000, Kim and O'Neill, 1997, Arthur and Anderson, 1983, Anderson and Arthur, 1983). Due to the lack of blocky calcite cement in the organic-rich lithofacies (1-3), we infer mild recrystallisation of the coccolith fragments has occurred due to their euhedral like shape under SEM-backscatter images (figure 3.1). Despite a later phase of carbonate recycling, this has not altered the δ¹³C signatures. δ¹⁸O values of -4 to -5‰ VPDB indicate equate to pore fluid temperatures to be 30-40°C (Anderson and Arthur, 1983, Kim and O'Neill, 1997). Pore fluids at cooler temperatures suggest carbonate cements precipitated when they were nearer the sediment water interface. With a mixture of isotopic signatures from marine and diagenetic sources, carbonate in the carbonate-rich lithofacies is interpreted to be derived from Late Cretaceous sea water and early microbiually mediated sulphate and iron reduction (Brigaud et al., 2008, Kim and O'Neil, 1997, Macquaker and Gawthorpe, 1993, Scotchman, 1991, Scotchman, 1989, Scotchman et al., 2000, Irwin, 1977).
A limitation of bulk isotopic compositions is the mixing of signatures from multiple phases of carbonate precipitation (Scotchman, 1989, Scotchman et al., 2000, Irwin, 1977). The issue is apparent in the organic-rich lithofacies (1-3) of the Eagle Ford Fmn where δ¹³C isotope values suggest an oxic marine source of carbonate, while δ¹⁸O values indicate a precipitation of carbonate during deeper burial. With petrological analysis and other geochemical techniques (Rock Eval) we can interpret a small quantity of carbonate has been precipitated early infilling foraminifera through anaerobic processes. The bulk of isotopic compositions are swayed by the dominant phase. In the case of the organic-rich lithofacies (1-3) isotopic signatures are derived from recrystallised coccolith fragments.

3.4.3 Gypsum

Gypsum is observed and measured from Eagle Ford Fmn samples from outcrop, but is not observed in core samples. It is measured in XRD but always below 1%. A common process is the oxidation of sulphate minerals, which precipitate gypsum (Moses and Herman, 1991). Pyrite is oxidised when exposed to water and oxygen. With the formation exposed at the surface, an infinite amount of water and oxygen is supplied to sulphide minerals. Calcite can neutralise the production of acidic environments, however this does not inhibit the precipitation of gypsum (Moses and Herman, 1991). Due to the high pyrite content of the Lower Eagle Ford Fmn, oxidation of pyrite is interpreted to be the source of gypsum in the Eagle Ford outcrops, via the following reaction:

\[
2\text{FeS}_2 + 3\text{CaCO}_3 + 9\text{H}_2\text{O} + 8\text{O}_2 = 2\text{Fe(OH)}_3 + 3\text{CaSO}_4\text{2H}_2\text{O} + \text{SO}_4^{2-} + \text{3CO}_2
\]  
(Reaction 4)

Gypsum in the Eagle Ford Fmn is interpreted to be a product of uplift and therefore is only observed in the outcrop. Gypsum is not present in the subsurface so is not a factor in burial diagenesis.

3.4.4 Mixed layer Illite/Smectite

A key difference between the organic-rich lithofacies (1-3) and the carbonate rich lithofacies (5-7) is clay volume. The organic-rich lithofacies, especially lithofacies 1 and 2, contain significant volumes of clay minerals (44% and 27% respectively) (table 3.1). The presence of clay minerals is important because they are highly

A significant proportion of the total clay fraction is mixed layer I/S (Figure 3.4). Abundances can vary throughout the formation between 22% and 65%, with an average of ~60%. Illite is consistently between 40-50% throughout the formation with kaolinite and chlorite forming the remainder of the total clay volume (Figure 3.4). There is little to no smectite, suggesting a complete transition to mixed layer I/S (Freed and Peacor, 1989, Bethke et al., 1986). The smectite to illite reaction has been described as a dissolution-precipitation reaction (Bethke et al., 1986, Freed and Peacor, 1989, Thyberg et al., 2010, Nadeau et al., 1985). Smectite particles dissolve and authigenic illite precipitates and grow, with excess Si released into the surrounding pore fluids (Nadeau et al., 1985, Thyberg et al., 2010, Worden et al., 2000b, Taylor and Macquaker, 2014, Peltonen et al., 2009, Oertel and Curtis, 1972, Mondol et al., 2008, Bethke et al., 1986). Reaction 5. Simplified equation from Boles and Franks 1979, illustrates the process:

\[
\text{Smectite} + K^+ = \text{Illite} + \text{Silica} + H_2O
\]

(Reaction 5)

The Smectite to illite reaction generally starts to take place in similar burial depths and temperatures to hydrocarbon generation, but can continue to metamorphism (Leo Lynch, 1997, Bethke et al., 1986, Freed and Peacor, 1989). Bar Si and H$_2$O, the reaction also gives off a wide range of minerals, such as: Mg, Fe, Al, Na and Ca. These mineral forming ions with the release of H$_2$O can precipitate minerals and cements such as quartz, calcium carbonate, dolomite, kaolinite and chlorite (Leo Lynch, 1997, Nadeau et al., 1985, Thyberg et al., 2010). A potassium source must be available for the reaction to occur (Boles and Franks, 1979). A likely source of potassium in fine-grained siliciclastic sediments is from the dissolution of K-feldspar (Boles and Franks, 1979, Thyberg et al., 2010, Freed and Peacor, 1989). However, feldspars are rarely observed under thin section or SEM in the Eagle Ford Fmn. The few feldspars that are observed are replaced with authigenic kaolinite and are only present in the organic-rich lithofacies (1-3) present in the Lower Eagle Ford Fmn. K-
feldspars are interpreted not to equate to the volume of potassium needed for the full smectite-illite conversion reaction throughout the Eagle Ford Fmn. We infer the bulk of potassium is sourced elsewhere, likely the organic material itself within the sediment (Kanaya and Katada, 1975, Robison, 1997). Potassium, along with uranium is one of the key elements detected in gamma ray logs used for identifying organic-rich sediment in the sub-surface (Kanaya and Katada, 1975, Robison, 1997). Therefore potassium is likely to be sourced from the organic-rich lithofacies in the Lower Eagle Ford Fmn. However it is uncertain where potassium is sourced in the Upper Eagle Ford Fmn, where quantities of organic matter are small (<1%).

3.3.5 Kaolinite


The presence of kaolinite cements within uncompacted planktonic and benthic foraminifera chambers in lithofacies 1-3, and to an extent lithofacies 5, indicates kaolinite was being precipitated relatively early during burial. This implies dissolved silicate and aluminium was present in the pore fluids during early diagenesis, prior to significant compaction in the Eagle Ford Fmn (Fein, 1994, Barcelona, 1980, Crossey, 1991). Organic acids such as carboxylic acid are the likely cause of Al-mobilisation within the pore water network, where reactive silicates were also present (Aplin et al., 2006, Barcelona, 1980). Reaction 6. Simplified equation illustrating kaolinite authigenesis.

\[
2\text{Al(OH)}_4^- + 2\text{Si(OH)}_4 + 2\text{H}^+ = \text{Al}_2\text{Si}_2\text{O}_5\text{(OH)}_4 + 7\text{H}_2\text{O}
\]

(Reaction 6)

The presence of kaolinite replacing feldspars in the organic-rich units of the Eagle Ford Fmn, suggests Al-rich amorphous material was dissolving creating a source for free Al ions in the assemblage for the precipitation of authigenic kaolinite. A key observation throughout the Eagle Ford Fmn where kaolinite has precipitated is, it is
not associated with the dissolution of foraminifera shells, coccolith fragments or other faunal debris. This implies that carbonate minerals were stable in the diagenetic system and were not the main acid-buffering minerals. The same observation is observed in the Kimmeridge Clay formation in the UK by Macquaker et al., 2014, Macquaker et al., 2002, Scotchman, 1989, Taylor et al., 2010. The same authors also state local clay dissolution of feldspars was acting as an acid buffer and as a source of Al and Si ions for kaolinite authigenesis.

### 3.4.6 Chlorite

Free, Si, Al, Mg and Fe ions are needed with suitable temperatures (<80°C) and pressures (30-40MPa) to precipitate chlorite in mudstones (Burton et al., 1987). Mg and Fe are interpreted to be sourced from the conversion reaction of smectite to mixed layer I/S and illite, releasing free Mg, Fe, Al, Na and Ca ions and H₂O into the surrounding pore network (Worden et al., 2000b, Niu et al., 2000, Nadeau et al., 1985, Mondol et al., 2008, Burton et al., 1987, Boles and Franks, 1979, Bethke et al., 1986). Chlorite has two suggested precipitation pathways in sedimentary formations: 1. Pseudomorphed from kaolinite to chlorite (chloritisation). 2. Precipitated from solution (Burton et al., 1987). The latter has been observed in modern Holocene mud deposits where the dissolution of smectitic clays and related soil-derived siliciclastics have been linked to the precipitation of chlorite (Mackin and Aller, 1984b, Mackin and R. C. Aller, 1984a, Aplin, 2000). Increased Fe and Mg ions within pore waters also drive the kaolinite to chlorite (chloritisation) reaction, where Fe/Mg replaces Al ions (Burton et al., 1987, Macquaker et al., 2014, Aplin, 2000). In the Eagle Ford Fmn, we only observed Fe-rich endmember (chamosite) of chlorite (figure 3.5). Reaction 7. Simplified equation illustrating chloritisation.

\[
\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 5\text{Fe}^+ = (\text{Fe}_5\text{Al})(\text{AlSi}_3\text{O}_{10})(\text{OH})_8
\]

(Reaction 7)

Despite the presence of poly-framboidal pyrite next to chlorite grains in the micritic matrix, we infer the source of Fe is from the smectite/illite conversion reaction, not from early diagenesis where Fe was sequestered into pyrite. The precipitation of chlorite is a late diagenetic process, while pyrite precipitation is one of the first. Pyrite framboids within foraminifera tests indicate that it was formed by the reduction of sulphate to sulphide (Al Balushi et al., 2013, Aplin and Macquaker,
Pyrite poly-framboids do not display dissolution under SEM. This apparent non-reactivity of pyrite implies Fe was almost certainly derived from a fluid phase oversaturated in iron during later burial at depth (Burton et al., 1987, Freed and Peacor, 1989, Aplin, 2000). Past authors have stated a relationship between increasing chlorite precipitation and depth (Aplin, 2000, Burton et al., 1987, Thyberg et al., 2010). Burton et al. 1987, state the onset of chlorite precipitation occurs in Gulf Coast mudstones at ~3,300ft depth. With some Eagle Ford Fmn wells at depths of up to 14,000ft, the expectation would be a significant chlorite fraction. In the Lower Eagle Ford Fmn, the abundance of chlorite is relatively constant regardless if the section is at 7,000ft or 13,000ft depth (figure 3.3). Implying there is a limit on the abundance of free Fe and therefore, a limit on chlorite precipitation. In the Upper Eagle Ford Fmn, despite buried in many areas beyond 3,330ft, there is no chlorite. Indicating the limiting factor for chlorite precipitation is the availability of Si, Al, Fe and Mg. Due to the decrease in total clay volume in the Upper Eagle Ford Fmn, we interpret that these key components were unavailable, or insufficient to precipitate chlorite, regardless of depth. Lower Eagle Ford Fmn samples containing chlorite have a depleted kaolinite volume compared to samples which do not, but have a similar total clay volume, indicating a significant quantity of chlorite is precipitated (pseudomorphed) from kaolinite (Worden et al., 2000b, Mondol et al., 2008, Burton et al., 1987, Bethke et al., 1986). Burton et al., 1987 found the same trend in fine grained Gulf Coast sediments.

3.4.7 Limitation of clay analysis and Authigenic vs Detrital Clay Mineral Compositions

For this study, all XRD was whole rock composition analysis. This type of analysis is accurate to 0.5-1% for carbonate minerals and other minerals like quartz, glauconite, pyrite and gypsum. However bulk mineral composition is only accurate to ~3 weight % for relative abundances of clay species (Weatherford, 2016). For bulk composition XRD, mineral atoms are randomly orientated. This procedure is fine for calcite, dolomite and quartz, but not clay minerals because clay minerals have similar X and Y dimensions. For accurate clay mineral identification and quantification, a clay mineral prepared sample is best where they are specifically orientated to increase basal reflection. This allows for a much better analysis of their
Si layers and creates a much more accurate form of analysis (Weatherford, 2016, SRODOI, 2001). Future work would ideally incorporate specific clay mineral XRD for the investigation.

The one piece of clay mineral XRD data from the Statoil/Talisman-1 core is a good dataset to evaluate general clay mineral distribution throughout the Eagle Ford Fmn (Figure 3.4). However, there is no detail to the log. There is no indication how long the well is, no depths indicated, and no stratigraphic markers. While there is a breakdown of individual clay minerals present, there is no indication of total quantities, just ratios and therefore does not give an accurate indication of clay content at any particular depth. This makes any conclusions regarding quantification of specific clay minerals difficult. While Statoil were happy to provide this dataset for analysis, they could not provide any other details.

Electron microscopy analysis and clay mineral XRD point towards suggests a significant amount of the clay volume in the Eagle Ford Fmn is authigenic. This is due to the complete transformation of smectite to illite/smectite (I/S), the precipitation of kaolinite in foraminifera and the precipitation of chlorite at deeper depths of burial. However some of the clay mineral assemblage could be detrital. Several factors can control the clay content of mudstones. They are; depositional mineralogy, environment and climate (detrital clay input); burial pressure and temperature, burial rate; changing pore-fluid compositions and hydrocarbon migration (Kantorowicz, 1984). While the Eagle Ford Fmn contains illite, kaolinite and chlorite that is interpreted to have formed through the dissolution of other, less stable alumino-silicates such as K-feldspars or smectite, a proportion of these minerals could be from detrital sources (Burton et al., 1987, Kantorowicz, 1984). There is strong evidence to support chlorite is 100% authigenic due to its distribution and appearance under SEM. However kaolinite and illite grains present in the matrix (Figure 3.5 and 3.6) are less conclusive. While both are interpreted to be authigenically sourced, some grains could be detrital. During the Late Cretaceous heightened volcanic activity is thought to have increased global CO₂ concentrations in the atmosphere assisting in creating a “super greenhouse climate” (Blakey, 2011, Arthur and Sageman, 2004, Corbett and Watkins, 2013). The super greenhouse climate was very humid and wet, ideal conditions for erosion of clay minerals to be transported from terrestrial to marine environments, via fluvial systems (Aplin et al.,
2006, Bethke et al., 1986, Boles and Franks, 1979, Burton et al., 1987, Kantorowicz, 1984, Michalopoulos and Aller, 2004). It is likely smectite and illite were sourced to the Eagle Ford Fmn from the interior. However smectite has been converted fully to 70% illite/smectite, giving the impression the vast majority of clay minerals are authigenically sourced. Illite however, can be sourced from both. Distinguishing between the two is difficult making it difficult for the author to pinpoint whether illite is detrital or authigenically sourced. Further work using clay mineral XRD analysis (instead of bulk rock composition) and a specific study petrological study using a SEM will help determine the sources of clay mineralogy in the Eagle Ford Fmn.

3.4.8 Quartz

Quartz cements in mudstones from re-crystallisation (Si remobilisation) of amorphous silica has been well documented (Schieber et al., 2000, Thyberg et al., 2010, Peltonen et al., 2009). However, quartz that is not identifiable as biogenically derived has been controversial for some time e.g., (Milliken, 1994). Recrystallised siliceous planktonic organisms are difficult to identify, especially since they are rarely observed in the Eagle Ford Fmn. Some siliceous organisms are present in the Eagle Ford Fmn, especially in lithofacies 6, where they are interpreted to be the remnants of radiolarians. All of these have undergone early dissolution and are replaced by authigenic calcite. The Si derived from dissolved radiolarians and other amorphous material containing Si (and opal A/CT), is believed to have driven kaolinite authigenisis during early diagenesis, as well as equant quartz cements which proceed carbonate cementation (Thyberg et al., 2010, Macquaker et al., 2014, Taylor and Macquaker, 2014). Thyberg et al 2010 describe similar quartz cement types in North Sea mudstones. They interpret most of the equant quartz cements present in North Sea mudstones were probably precipitated before substantial amounts of smectite was converted to illite. This is because high Si saturation of pore waters produced by amorphous Si, stabilises smectite before the transition to illite (Thyberg et al., 2010, Thyberg and Jahren, 2011, Peltonen et al., 2009, Freed and Peacor, 1989). The illitisation reaction requires silica saturation where quartz is soluble (Egeberg and Aagaard, 1989). This indicates, that equant quartz cements, pre-date the mirco-cements in the micritic matix and the precipitation of equant quartz gradually reduce the concentration of Si in the pore waters. Smectite then
becomes unstable and the clay conversion reaction begins (see Reaction 4). Authigenic micro-pore filling quartz cements are interpreted to correspond to the onset of the smectite-illite conversion reaction. Micro-pore filling cements are interpreted to be sourced from free Si ions released from the clay mineral reaction (Boles and Franks, 1979, Thyberg et al., 2010, Schieber et al., 2000). As mentioned above, the smectite to illite reaction results in significant amounts of free Si in the surrounding pore waters. Excess silica quickly precipitates as quartz near to or next to the smectite-illite crystals. Various authors state pore waters with high Si concentrations precipitate small micro-pore cements at temperatures where smectite is converted to illite (70-80°C) (Schieber et al., 2000, Milliken, 1994, Williams et al., 1985, Thyberg et al., 2010). This is also interpreted to be one of the possible factors that limit chlorite precipitation later in diagenesis, as most of the Si is sequestered in authigenic quartz.

3.5 Conclusions

Combined optical, electron microscopy of 78, 20µm cut thin sections and geochemical analysis reveal a wide range of diagenetic processes in the Eagle Ford Fmn. We show that early microbial mediated diagenetic reactions and deep-burial processes have a big impact on the mineralogical composition of mudstones. Early and late burial processes are both key in the Lower Eagle Ford Fmn. In the Lower Eagle Ford Fmn non-ferroan, calcite cements and frambooidal pyrite infill planktonic foraminifera. Kaolinite is precipitated during early diagenesis via available Si through dissolution of biogenic Si tests and the organic acids mobilising Al from the decay of organic matter. Coccolith fragments constitute the majority of the carbonate in the Lower Eagle Ford and are mildly recrystallised at depth. Smectite is fully converted to 70-80% mixed layer I/S providing ions such as Si, Fe and Al for the precipitation of authigenic quartz and chlorite. Anoxic conditions only allow a small portion of organic material to be oxidised, allowing for TOC values <4% throughout the Lower Eagle Ford Fmn, with some values as high as 7-8%.

In contrast the Upper Eagle Ford is mainly impacted by early and syn-depositional processes. Aerobic oxidation of organic matter reduces the amount of TOC observed in the Upper Eagle Ford Fm. Further microbial processes precipitate extensive non-ferroan, zoned, calcite cements which infill and surround biogenic debris.
Burrowing, the presence of a variety of fauna (including benthic foraminifera) all suggest oxygenated marine conditions.

This study shows that mudstones can result in contrasting mineralogical and geochemical compositions due to diagenesis. Detailed observations through optical and electron microscopy can advance our knowledge of early and late diagenetic pathways in mudstones and are vital tools for predication for unconventional reservoir exploitation.
4. The origin of concretions and limestone beds in the Lower Eagle Ford Formation
4.1 Introduction

Regular, lateral cyclic alterations of organic-rich mudstone and limestone beds/concretions, on a sub-metre (concretion) to >1km scale are a common feature in the organic-rich section of the Lower Eagle Ford Fmn (Dawson and Almon, 2010, Dawson, 1997, Liro et al., 1994, Donovan et al., 2012). These features, especially the >1km limestone beds are of particular interest because they are likely to compartmentalise the Lower Eagle Ford Fmn, acting as baffles impacting recovery during production. The origin of these concretion/limestone features remains unclear (Dawson, 1997, Dawson and Almon, 2010, Donovan et al., 2012). These features are also of interest because; the sub metre (football concretions) are visually unusual and give the impression they do not belong in the surrounding organic-rich mudstone. When observing the outcrops, the first question that arises is, “why are these features present?” The nature of the limestone beds and the features present surrounding them suggest primary processes could have had an effect on diagenesis and therefore the final composition of the Lower Eagle Ford Fmn in the sub-surface.

This chapter aims to unravel the diagenesis of lateral sub-metre (football concretions) to >1km scale limestone beds that are observed in the organic-rich, clay-rich, Lower Eagle Ford Fmn outcrops in west Texas, USA. These features may contain further information on not only the effects of burial diagenesis, but also how variations in primary processes effected the burial of the Lower Eagle Ford Fmn. Due to the lateral sub-metre (football concretions) to >1km scale limestone beds size and location, these features are relatively easy to study with all samples collected from the outcrops in south-west Texas (Figure 4.0).

The aims are: 1) To discover which mechanism(s) created the localised sub-metre concretions within the organic-rich mudstone. 2) Discover if the lateral extensive >1km limestone beds, varying from 5-35cm thick, are an amalgamation through continued growth of sub-metre concretions found in other horizons. Or are they a product from a completely different set of processes? (i.e. variations in the deposition environment, such as the complete shutdown of sediment supply or the oxygenation of the water column, and/or bottom waters).
4.2. Methods

4.2.1 Outcrop and sample locality

To investigate the organic-rich mudstone/limestone cycles of the Eagle Ford Fmn, I am going to focus on a specific stratigraphic unit of the Lower Eagle Ford Fmn known as Facies B (Donovan et al., 2012). Facies B consists mainly of organic-rich mudstones (Weakly Laminated Mudstones, lithofacies 2) with a carbonate content of ~47% and has excellent source rock properties (TOC% values of 6.2% and HI of 700mgHC in places) (Donovan et al., 2012). Within this unit are distinct sub-metre concretions along particular horizons and continuous limestone beds along others. All rock samples were collected from a road cut exposing the Eagle Ford Fmn along Highway 90, west Texas, approximately 50 miles west of the border town Del Rio (figure 4.0). Facies B is well exposed near the little settlement of Cumstock on U.S Highway 90 (29.379700, -101.203867) and allows easy access for rock sampling and logging.

Key features such as spherical concretions were fairly easy to distinguish in outcrop due to their shape and distribution. Carbonate rich horizons were harder to recognise because the outcrops were all one colour due to the effects of weathering. Closer analysis of the outcrops in the field revealed the limestone beds within the organic-rich mudstones. 46 samples were selected for analysis from the Eagle Ford Fmn outcrops. 17 samples were drill plugs. The other 29 were rock samples carefully hammered out of the outcrop. Some samples were specifically selected where little weathering had taken place. Other samples were cored from highly weathered areas as this made mudstone, spherical concretions and limestones easy to distinguish. This is so mineralogical and geochemical analysis could be done on samples that were clearly different giving a ‘base’ as weathering does not affect these components. Prior to thin section preparation specimens were studied and any sedimentary features were recorded. Thin sections were made from all samples regardless of weathering.
Bore holes drilled for He porosimetry measurements. Location:
Lat: 29.379714
Long: -101.203864

Bore holes drilled for He porosimetry measurements, thin section and XRD analysis. Location:
Lat: 29.379709, Long: -101.203865
Figure 4.0. A. Map of west Texas along showing the location of the Eagle Ford Formation outcrops northwest of Del Rio (yellow square). B. Satellite image showing Del Rio and U.S. Highway 90, the town of Cumstock and the location of the outcrops studied (west of Comstock). (Yellow square). Coordinates are 29.379700, -101.203867. C. Photograph of the outcrops (road cuts) that run parallel with U.S Highway 90. All samples collected in this study are within this view. D. Photograph facing west of the roadcut outcrops along Highway 90. (Coordinates Lat: 29.379700, Long: -101.203867). E. Location of 6 core plugs taken from the north facing outcrop along Highway 90 for He porosimetry measurements, (coordinates, Lat: 29.379714, Long: -101.203864. F. Additional core plugs taken from the south facing outcrop along Highway 90 for He porosimetry, thin section and XRD analysis (Coordinates, Lat: 29.379709, Long: -101.203865).

4.2.2 Analytical techniques

Geochemical analysis (isotopic C and O compositions), along with microscopic observations through polarised light microscopy and electron microscopy form the bases of this study along with XRD and macroscopic observations from outcrop and some core.

Macroscopic observations of the outcrops took place along Highway 90 where samples were collected US. 15 core plugs were extracted from the outcrops using a core plugger (figure 4.1). 17 rock samples were also collected including an entire spherical concretion. All samples were taken for petrological, mineralogical and geochemical analysis. All samples were carefully cut and prepared at Statoil ASA, Bergen, so all three analysis techniques could be conducted on the same material to identify composition and diagenetic history.

Figure 4.1. A. Facies B on Highway 90, west Texas containing weathered organic rich mudstones with interbedded concretions (1.70m person for scale). Bore holes show sample location and how samples were
sampled with the core plugger (GPS location: 29.379709, -101203865). Rock samples were extracted using a rock hammer. 

**B.** Organic rich marl from Facies B in core (Leppard 1-H) at the Bureau of Economic Geology (BEG), Austin, Texas. Note, the difference in colour of the organic rich marl before weathering.

Two cores (Briggs Ranch and Lark Ranch cores) belonging to Statoil and Talisman Energy were sampled for petrographic and geochemical analysis. Five samples were taken from these cores for petrological, mineralogical and geochemical analysis.

**Petrographic analysis**

40 thin sections were prepared at Statoil ASA, Bergen. All thin sections were scanned using a flatbed scanner (Cannon CanoScan 5600F), generating high quality whole thin section images. Each thin section was then analysed under low to medium resolutions (10^{-3} to 10^{-4} m scale) under transmitted light (TL) in both plane polarised light (PPL) and cross polarised light (XPL) using a Nikon Optiphot2-Pol petrographic microscope. Examination of the thin sections under XPL was of little help due to the nature of high interference colours when the thin section is cut too thin. On top of the microscope viewing the thin sections was a Jenoptik jena-07739 digital camera allowing photomicrographs to be taken. A CITL Cathodoluminescence Unit (Model CCL 8200 mk3) was used alongside an Olympus BH-2 petrographic microscope, with both utilising a digital camera (Jenoptik jena-07739) to capture micrographs in CL and PPL. Operating conditions for the CL were approximately 20kv (cathode voltage), 300 µA electron beam current and 0.2 torr vacuum.

Petrographic, diageneric and compositional information were obtained from these techniques. After TL and CL investigations 15 of thin sections were selected and carbon coated for electron optical analysis to examine the, composition and diageneric fabrics and other constitutes at higher resolution (10^{-5} to 10^{-6} m scale). A JEOL 6400 scanning electron microscope (SEM) with a solid-state, Link Systems 4-quadrant backscattered (BSE) detector was used to analyse the thin sections. Operating conditions for the SEM were 20kv, 2nA and a 15mm working distance. BSE micrographs were recorded and projected by a Semafore digital framestore installed into the SEM. A semi-quantitative, energy dispersive X-ray system determined major element compositions of minerals (Fe, Si, Ca, Mg, S, K, P and Al). Identifying mineral composition was crucial to discriminate and geochemically quantify diageneric phases of carbonate and other minerals.
Mineralogical and geochemical analysis

Qualitative and quantitative mineral composition of the Eagle Ford Fmn was determined by 40 bulk samples, which were analysed by a X-ray diffractometer (XRD). A Philips PW1730 X-ray diffractometer (Cu Ka radiation) analysed the 17 samples operating a tube voltage of 40 kV and a tube current of 20 mA, a step size of 0.01° and a time constant of 2 s. For each sample, a smear was prepared by mixing 0.5 g of the sample with two drops of amyl acetate and leaving it to dry on a glass slide. Once dried the slide was placed into the XRD. Semi-quantitative estimations of bulk-mineralogy fractions were carried out using peak area measurements. To establish a better understanding of mineral composition (quantification), further analysis was conducted using the program TOPAS developed by Bruker. TOPAS is a quantitative program that analyses the peak areas but factors in the diffraction coefficients of the elements identified. The pattern fitting of the peaks and coefficients in TOPAS was good for the Eagle Ford Fmn samples so the mineral quantities should be close to reality. A hand-held XRF was also used to help determine the elemental composition of some of the samples collected in outcrop.

Stable carbon and oxygen isotope analysis was performed on the same (whole rock) 40 samples that were analysed by XRD. All 40 samples were subject to a cold methanol:dichloromethane (1:9 solvent) extraction at room temperature using an ultrasonic water bath to remove the organic content. To separate the sample and solvent they were centrifuged and then left in a fume cupboard over night to dry and let any excess solvent to evaporate. The samples were inserted into a VG SIRA-12; gas sourced mass spectrometer (MS) in the University of Liverpool Stable Isotope Laboratory, UK. Here, $^{13}$C/$^{12}$C and $^{18}$O/$^{16}$O ratios were measured. All results and ratios are presented by the standard delta ($\delta$) as parts per mill ($\‰$) from the Vienna Pee Dee Belemnite (VPDB) international standard.

4.3 Results

All samples from the facies B outcrops, the Briggs Ranch and Lark Ranch cores are organic-rich weakly laminated mudstones, concretions or limestone beds. The organic-rich weakly laminated mudstones are easy to identify in both outcrop and core. In outcrop the organic-rich weakly laminated mudstones are fissile, soft and more weathered compared to
the harder concretions, which protrude out of the outcrop face. In core they are black and weakly laminated (figure 4.1). The concretions in core are grey in colour and mostly massive (figure 4.2). Although some contain ripple laminations and cross beds. There are four main types of concretion that have been identified in the Eagle Ford Fm outcrops. They have been classified as Type 1, 2, 3 and 4 respectively (figure 4.4). Despite being easy to identify concretion/limestone beds in core due to their colour, it is impossible to determine which type of concretion was present due to the lack of lateral spatial resolution. Concretion classification is therefore entirely based from outcrop studies (fig. 4.2).

1. Type 1 is a continuous limestone bed that extends along the entire outcrop (>1km long). The bed is 20-30cm thick. A volcanic ash bed (bentonite) is directly beneath the cemented bed. There are other continuous limestone beds in the outcrops however they were inaccessible for sampling (figure 4.3).

2. Type 2 concretions are called in this study “footballs” as they resemble American Footballs in appearance. They are isolated and occur every ~5-10m above a volcanic ash bed and are surrounded by organic rich mudstone. They have a clear core and outer shell when broken open with a rock hammer. The footballs are commonly >50cm long, 20-30cm high and 20cm wide (figure 4.3).

3. Type 3 concretions are lenticular, elliptical concretions that are no larger than 10cm thick, but vary in length. Some concretions are <50cm while others can be >1.5m long. Their y axis dimension and how far they extend into the outcrop is unknown. This type of concretion contains ripple laminae and cross trough stratification (figure 4.3).

4. Type 4 concretions are a thin continuous bed of limestone (~10cm) similar to Type 1 but ‘pulse’ in localised areas to a thickness of ~30cm. They are thin, elongated, and elliptical in shape similar to Type 3 concretions; however they are connected by a thin strand of limestone that runs continuously throughout the outcrop. This type of concretion contains ripple laminae and cross trough stratification (figure 4.3).

4.3.1 Organic-rich weakly laminated mudstones

The organic-rich weakly laminated mudstones display little features or structures in outcrop bar planar laminations where weathering has not been so destructive. In core and thin section the organic rich mudstones are mainly black, black-brown in colour (figures 4.2 and 4.3). The organic rich mudstones are mainly observed in the lower Eagle Ford Fm. Planktonic foraminifera are common and are the main silt sized (>62.5µm) component
found in the organic rich mudstones along with fragmented inoceramids bivalves. Larger specimens are visible in core. Both are found mainly in sub millimetre to millimetre scale planar laminae and are intact and show little signs of compaction, although the foraminifera within them do display some damage to their shells, caused by recrystallisation and micritisation. Some laminae are truncated or contain wavy ripples, although the latter are rare. Pyrite and phosphate grains are less common but are always present in thin section.

Figure 4.2. A. Concretions in outcrop. B. The edge of a concretion in core (red circle). The light grey section below the concretion (red circle) could be a concretion, but remains unknown. Planar laminae are present in the concretions which consist of foraminifera. GPS location 29.3793, -101.2038. See figure 4.0 for map of location.

Thin section and SEM analysis with XRD data shows calcium carbonate (CaCO₃), authigenic clay (mixed layer I/S, kaolinite), authigenic quartz and organic matter are the main components of the organic-rich weakly laminated mudstones (see Figure 4.4 and Table 4.1). Silt sized material (>62.5µm) is common and consists mainly of planktonic foraminifers and inoceramid bivalves. Clay minerals are common in thin section with wispy mixed layer I/S seen within the matrix of every thin section of the organic-rich weakly laminated mudstones. Authigenic kaolinite is also common within foraminifera chambers and in the micritic matrix. Authigenic quartz grains are common but are only observed under SEM. Organic matter is abundant in thin sections sampled from core but is
not present in thin sections from the outcrops. This is due to the nature of the samples collected at a location where weathering is prolific.

Despite the quantity of carbonate precipitation, the ability to preserve organic matter has not been significantly impeded, as the Lower Eagle Ford Fm is highly organic and classified as an excellent source rock. Traversing up through the stratigraphy, CaCO₃ content increases. Concretion and limestone beds increase in occurrence. However TOC values decrease only a little (~1%) with the entire Lower Eagle Ford classified organic-rich. Carbonate within the organic rich mudstones has isotopic δ¹³C values between 0 and 1 ‰ (average δ¹³C 0.63‰VPDB) and δ¹⁸O values between -7 and -8 ‰ (average δ¹⁸O - 7.27‰VPDB).

4.3.2 Concretions

The concretions are distinctive and easy to identify in core due to their light-grey to grey colour. Extensive cementation produces a homogenised looking rock that varies little in colour and composition. Planar laminations are present in most samples although a few samples contain weak laminations and look massive, but it is stressed this is rare. Sharp contacts are present at the top and bottom of most concretions. Floating planktonic foraminifera are common but difficult to spot due to the facies colour. With a hand lens the larger specimens that are intact can be seen within the calcareous matrix. Planktonic foraminifera are common and are the main silt sized (>62.5µm) component found in this facies. Both are found mainly in sub millimetre to millimetre scale planar laminae. Some laminae are truncated or contain wavy ripples, although the latter are rare in core. In outcrop the concretions are easy to identify as they are less weathered and stick out of the formation compared to the organic rich mudstones due to their hardness. Sedimentary features are common in most of the concretions in outcrop and include; low angle cross stratification, trough cross-stratification, low angle foresets, steep foresets, and planar bedding. Some laminations are present but only in parts of certain concretions.

The concretions contain significantly more CaCO₃ compared to the organic rich mudstones. XRD (table 4.1) shows that the concretions can contain up to 90% CaCO₃ with values falling between 75-90% CaCO₃. The remaining composition is mainly quartz ~6%, plagioclase ~1.3% and K-feldspar 0.7%. TOC values for this facies are low compared to the organic rich mudstones, with average values typically ~1%.
Figure 4.3. Outcrop photographs containing all the types of concretions identified in facies B. A. Photograph, looking towards the south east at the north facing outcrop (road cut) that exposes facies B along U.S Highway 90, west of Comstock, Texas (Coordinates are 29.379700, -101.203867). B. Identical photograph to A, with red polygons highlighting the location and nature of the concretion types. Type 1 -
continuous 20-30cm thick limestone bed that runs throughout the outcrop (>1km). An ash bed lies directly beneath it (purple). Type 2 concretions are the distinct football-like concretions that occur every 4-5m below type 1 with an ash bed sitting directly below them. 1m below the type 2 concretions are the elliptical type 3 concretions. The type 4 concretions sit 30cm below the type 3 concretions with a distinct ash bed directly below it.

4.3.3 Type 1

Three samples (A1, CP2 and CP3) were extracted from a type 1 concretion in outcrop (fig. 4.3). The samples were extracted from one area where the bed was easy to access. The type 1 concretions are typically 20-30cm thick, massive and contain few sedimentary features in outcrop, bar planar laminations and sub-horizontal laminations. They display sharp contacts with the organic rich mudstones above and the bentonite below. The thickness of the bed remains consistent throughout the >1km long outcrop (figure 4.3). In thin section the type 1 concretions are dominated by recrystallized equant, angular to sub-angular cement grains with a micritic matrix between grains (figure 4.4). Some areas between calcite cements are clay rich figure 4.4). Cement grain sizes vary between 20-50µm with little biogenic material present. Foraminifera are observed but rare. All are infilled with calcite with their shells recrystallised and some micritised. Some foraminifera are completely recrystallised and a degree of carbonate mobilisation has occurred as foraminifera are damaged, mis-shaped and have cements attached and surrounding their shells. Radiolarians are common in thin section but all are fragmented and calcified and are approximately 300-500µm in diameter. CL shows non-ferroan calcite cement containing zoning. Cements are bright throughout the matrix. In CL biogenic debris are easier to identify (figure 4.4). The remnants of foraminifera and inoceramid bivalves display bright fluorescing cements. The matrix containing clay minerals is generally duller (figure 4.4). Electron microscopy shows the extensive cementation in the type 1 concretions by equant calcite cements. Between the cements is a micritic matrix consisting mainly of kaolinite, micron quartz cements, coccolith fragments, mixed layer I/S and kaolinite (figure 4.4). XRD shows carbonate content of the type 1 concretions is approximately 90%. Almost all of the carbonate is found as equant cement grains, with 1-2% found as coccolith fragments present as matrix between the cement grains. Quartz and kaolinite are the only other minerals found in any significant quantity, with kaolinite being the most common mineral found between carbonate cements. Isotope analysis reveals the type 1 concretions have an
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Table 4.1. XRD showing the composition of all samples extracted from the outcrops. D1S1 = day and stop number. ML = middle layer (or) LL = lower layer. C = concretion. M = marl. L1 = marl below (lower) concretion and sample number. U1 = marl above (upper) concretion and sample number. F = football like concretions in outcrop and sample number.
Figure 4.4: A. Sample D1S1-ML-M-U1. Thin section micrograph of a weakly laminated foraminiferal mudstone illustrating sub-mm scale ripples, organic rich mud drapes (MD), planktonic foraminifera (F) infilled with calcite cement. Fecal pellets (FP) are aligned with laminae and contain randomly orientated calcite and clay mineral grains. Inoceramid fragments replaced by calcite are also a common feature in the weakly laminated foraminiferal mudstones. Scale bar 500µm. B. Thin section micrograph: identical image of A but in CL showing the dull, non-ferroan calcite carbonate within the matrix of the weakly laminated foraminiferal mudstone. Foraminifera’s (green circle) and fecal pellets (yellow arrow) contain brighter luminescing cements compared to the rest of the matrix, suggesting a different source of cement. Scale bar 500µm. C. SEM-BSE micrograph of a weakly laminated mudstone (sample Leppard 13665.30). Coccolith fragments (CC) constitute the bulk of the micritic matrix and display mild recrystallisation. Authigenic micro-quartz cements (Q) post-date the coccolith fragments. Mixed layer I/S (I/S) is also a common clay mineral present. D. Sample A1. Thin section micrograph of a Type 1 concretion. Scale bar 500µm. 20-50µm cement grains dominate the assemblage with little biogenic material present. E. Sample A1. Thin section micrograph of a Type 1 concretion illustrating the extent of equant calcite cements (EC) overprinting the original matrix. The remnants of foraminifera (RF) are difficult to identify in polarised light due to fragmentation but some foraminifera (F) remain intact and infilled and surrounded by calcite cements. Scale bar 500µm. F. SEM-BSE micrograph (sample 2279981), of a Type 1 concretion – displaying equant calcite cement grains (C). Inter-porosity is infilled with spherical micro-quartz cements (Q) and other clay minerals: mainly mixed layer I/S and kaolinite. G. Sample D1S1-ML-C1. Thin section micrograph of a Type 1 concretion. Scale bar 100µm. Two 500µm diameter calcified and fragmented radiolarians (RD). H. Sample D1S1-ML-MB1 in CL. Thin section micrograph of a Type 1 concretion. Scale bar 1000µm. 20-5050µm cement grains dominate the assemblage with 500µm calcified radiolarians displaying non-ferroan calcite cements containing zonations. Brighter cements are observed at the edges of cement grains.

average composition of $\delta^{13}$C -1.55‰ and $\delta^{18}$O -5.59‰ (A1: $\delta^{13}$C -1.26‰, $\delta^{18}$O -5.59‰ CP2: $\delta^{13}$C –1.72‰, $\delta^{18}$O -5.89‰ CP3: $\delta^{13}$C -1.66‰, $\delta^{18}$O -5.81‰ (figure 4.7).

### 4.3.4 Type 2

In outcrop the type 2 concretions resemble American Footballs due to their shape and size (figure 4.3 and 4.5). The type 2 concretions commonly display sharp contacts with the organic rich mudstones surrounding them and the bentonite bed immediately below. The type 2 concretions do not display any other sedimentary features in outcrop. Three rock samples (F1, F2 and F3) were extracted from a type 2, “football” concretion. F1 and F2 were sampled from the edge of a concretion left in situ, with F3 sourced nearer the centre. An entire concretion was also extracted (transect sections B1-B6, see table 4.1 & 4.2) from outcrop and transported back to Manchester for analysis. A transect from one edge to the other was made with several thin sections made every 7-8cm, along with samples for XRD.
and geochemical analysis to help understand how the concretions evolved during burial (figure 4.5).

In thin section F1 and F2 are similar in composition and texture and distinct compared to F3 (figure 4.7). F1 and F2 contain an angular grain texture. Grain sizes are (50-80µm) (figure 4.7). No biogenic material is observed. CL displays non-ferroan calcite cements with zoning. Cements are duller in the centre and brighten towards the edge of the grains. The matrix containing clay minerals and coccolith fragments is brown to black (figure 4.7). F1 contained a Mn content of 0.13ppm and Fe 313ppm. F3 is composed of finer grained calcite (20-40µm), compared to F1 and F2 (figure 4.7). Grains are angular to sub angular. Like F1 and F2 little biotic material is present in F3. Small foraminifera are observed, but are rare. Most foraminifera are entirely recrystallised while others that remain intact are infilled with calcite cement (figure 4.7). Both recrystallised and infilled foraminifera can be fragmented. CL displays non-ferroan calcite cements containing small levels of zoning towards the edges of cement grains. F3 contained a Mn content of 349ppm and Fe 0.18ppm.

Figure 4.5. Diagram of the Type 2 concretion split into six sections used for petrological and geochemical analysis. The transect begins at B1 and travels through the centre of the concretion to the other side at B6. B4 is the centre of concretion with a vertical thin section (B4-IV) sampled in the centre. A horizontal thin section (B4-3H) was also sampled in the centre of B4. An additional thin section (B4-2V) was also sampled from B4 at the top edge of the concretion, but near the centre to understand concretion morphology and growth. For each thin section, XRD and bulk stable isotope analysis was undertaken.
Figure 4.6. Cross-plot showing all the carbon and oxygen stable isotope compositions from Table 1. The black squares refer to organic rich mudstones sampled from outcrops between Type 3 and Type 4 concretions. The red squares refer to the Type 3 concretions, and green Type 4. The samples from the Football concretions (Type 2) are grey, orange and purple respectively.
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</tbody>
</table>

Table 4.2. Isotopic compositions showing the composition of all samples extracted from the outcrops. $D1S1$ = day and stop number. $ML$ = middle layer (or) $LL$ = lower layer. $C$ = concretion. $M$ = marl. $L1$ = marl below (lower) concretion and sample number. $U1$ = marl above (upper) concretion and sample number. $F$ = football like concretions in outcrop and sample number.
Figure 4.7. A. Thin section micrograph of type 2 concretion F1 (edge of concretion) illustrating equant calcite cement grains 50-80µm. The matrix is seen commonly surrounding individual cement grains. Foraminifera are difficult to identify to recrystallisation and fragmentation. Scale bar 500µm. B. Thin section micrograph; identical image of A but in CL showing the dull, non-ferroan calcite cements found in the edge of a type 2 concretion (F1). Cement grains contain zoning with dull centres and brighter fluorescing edges (white arrow). Some cements (green circle) fluoresce brighter that look to have precipitated after the original grains. Scale bar 500µm. The matrix remains brown to black (yellow arrow). C. Thin section micrograph of type 2 concretion F3 (near centre of concretion) showing the finer calcite grains (20-40µm) compared to F1 and F2. More calcite is present and less matrix compared to the F1 and F2. Foraminifera are difficult to identify as they are recrystallised, fragmented and have calcite grains surrounding and attached to them (white circle). D. Thin section micrograph; identical image of E but in CL showing non-ferroan calcite cements observed nearer the centre of a type 2 concretion (F3). Cement grains contain zoning with dull centres and brighter fluorescing edges (white arrow). Foraminifera are easier to spot in CL (green circle) due to their brighter fluorescence. E. Thin section micrograph of sample B1, displaying 50-100µm cement grains (yellow arrow) and intact foraminifera (F). A matrix composed of clay minerals, quartz and coccolith fragments infill inter-porosity between grains (orange arrow). F. CL image of sample B1 displaying bright, non-ferroan calcite cements that contain little zoning. Foraminifera (F) contain bright fluorescing cements. Some foraminifera have their shells micritised (white arrow). The matrix remains dull (green arrow). G. Thin section micrograph of B2 displaying 20-40µm angular cement grains. Foraminifera are common (F). Clay minerals (mixed layer I/S, kaolinite) quartz and coccolith fragments constitute the matrix which infills inter-porosity between the cement grains (green arrow). H. Thin section micrograph of B2 displaying 20-40µm cement grains, foraminifera (F) and a matrix infilled pellet (green circle).

Foraminifera contain brighter fluorescing calcite compared to the rest of the cement grains. Kaolinite is also present in the matrix. XRD results show the centre of the concretion is composed of more calcite and less quartz compared to the edges (table 4.1).

The Type 2 concretions have a distinct isotopic composition compared to the organic rich mudstones and other concretion types (figure 4.6). Their δ¹³C ratios are isotopically lighter than the other concretion types with the centre of the concretion being the lightest. Their δ¹⁸O ratios are also isotopically heavier compared to the weakly laminated mudstones and type 1 concretions (limestone bed). F1: δ¹³C -1.44‰, δ¹⁸O -4.93‰. F2: δ¹³C -1.35‰, δ¹⁸O -5.05‰. F3: δ¹³C -1.87‰, δ¹⁸O -4.48‰ (table 4.2 and figure 4.6)

Samples B1-B6 are from a transect running through an entire concretion extracted from outcrop. B1 is from the edge of the concretion- like F1 and F2 from a separate football concretion. B1 is dominated by angular recrystallised calcite cement grains and have precipitated against one another (figure 4.7). XRD shows calcite content is 89%. Some grains cross cut one another but this is rare. Grain sizes are 50-100µm (figure 4.7). Foraminifers are common - all are infilled with calcite and are larger than 100µm in diameter. Most have lost their shell walls to
recrystallisation, but some remain with their original shell walls with minor mictrisation (figure 4.7). Electrical microscopy shows a micritic rich matrix composed of coccolith fragments, kaolinite and quartz infills porosity between calcite grains. No radiolarians are present in the edge of the concretion. B1 has isotopic values of $\delta^{13}C$ -2.14‰, $\delta^{18}O$ –5.02‰, while B2 has isotopic values of $\delta^{13}C$ –1.95‰, $\delta^{18}O$ –4.51‰ (table 4.2 and figure 4.6).

B2 and B3 are samples heading towards the centre of the concretion (figures 4.5). XRD shows calcite content increases towards the centre of the concretion (92.4% and 93.3% respectively) (table 4.1). The recrystallised cement grains are finer grained compared to B1. In B2 the bulk of the calcite cements are 20-40µm. Larger cement grains are present but rare and can be up to 90µm long. Like B1, B2 contains a micritic matrix between calcite cements. Clay rich peloids/pellets are present surrounded by a recrystallised wall of calcite between calcite crystals. Micrite, kaolinite, mixed layer I/S and authigenic quartz cements are the main constitutes of the pellets (figure 4.8). No pyrite is observed in thin section or in XRD (table 4.2 and figure 4.6).

B3 contains finer calcite cements than B2. The bulk of cement grains are 1-15µm and are completely recrystallised (figure 4.9). Larger grains are present but do not exceed 50µm. Foraminifera are smaller compared to B2 and B1 (50-80µm diameter). CL shows they contain brighter luminescing cements compared to the duller non-ferroan cements that surround them. Like B1 and B2, electrical microscopy shows a micritic rich matrix composed of coccolith fragments, kaolinite and quartz infilling porosity between calcite grains. Peloids/pellets are present containing Micrite, kaolinite, mixed layer I/S and authigenic quartz, but unlike the peloids/pellets in B3, are not surrounded by a recrystallised wall/shell. B3 contains isotopic compositions of $\delta^{13}C$ –8.61‰, $\delta^{18}O$ –3.54‰ (table 4.2 and figure 4.6).

B4 is the centre of the concretion. A vertical and a horizontal thin section were sampled from the centre (B4-1V and B4-3H respectively), with a third thin section sampled at the top, near the centre upper edge of the concretion (B4-2V) (figure 4.5).

B4-1V is the vertical thin section sampled from the centre of the concretion. Recrystallisation has taken place with the bulk of the carbonate cement grains 1-10µm.
Figure 4.8. PPL, CL and SEM micrographs of a Type 2 concretion. A. Thin section micrograph of B3 displaying 1-15µm calcite cement grains. Foraminifera (F) are difficult to identify but are infilled, often fragmented and have their shell walls recrystallised. B. CL image of sample B3 displaying bright, non-ferroan calcite cements. Foraminifera (F) are easier to spot due to the recrystallisation of their shell walls. The micritic matrix (M) containing clay displays a blueish colour. C. SEM-BSE micrograph of sample B3 focusing on the micritic matrix between calcite cements (C). Kaolinite (K), along with coccolith fragments (CC), quartz (Q) are common. In this particular sample kaolinite dominates the matrix giving a blue luminescence is CL. D. Plane polarised thin section micrograph of B4-1V displaying recrystallised 1-10µm calcite cement grains. Foraminifera (F) are common, but are completely recrystallised and fragmented. Some matrix (M) is present between cement grains displaying a brown-black colour. E. Plane polarised thin section micrograph of B4-3H displaying recrystallised 1-10µm calcite cement grains. Foraminifera (F) are common, but are completely fragmented. F. Plane polarised thin section micrograph of B5 displaying recrystallised 1-15µm cement grains. Fragmented foraminifera (F) are common. Matrix infilled pellets/peloids are common in B5. Clay content within the matrix is displayed in C and H. G. Plane polarised thin section micrograph of B6 displaying recrystallised 50-100µm cement grains. No foraminifera or other biogenic material is visible in this sample. The micritic matrix (M) infills intergranular-porosity between calcite cements grains. H. SEM-BSE micrograph of sample B6 focusing on the micritic matrix between calcite cements (C). Kaolinite (K), along with coccolith fragments (CC), quartz (Q) are common.

XRD indicates calcite content is 90% (table 4.1). Quartz content, like B3 is low at 1-2%. Kaolinite is the main clay mineral. Electron microscopy shows kaolinite is found between calcite cement grains. Planktonic foraminifera are infilled, preserved and then fragmented with calcite cements (figure 4.8). CL displays mild micritisation and recrystallisation has occurred on their shell walls. The foraminifera also contain brighter cements compared to the surrounding cement grains. B4-1V has isotopic values of δ¹³C –6.96‰, δ¹⁸O –4.20‰ (table 4.2 and figure 4.6).

B4-3H is the horizontal thin section and is completely recrystallised with very fine calcite cement (figure 4.8). The bulk of calcite grains are 1-10µm. XRD indicates calcite content is 93.9% (table 4.1). Like B4-1V, forams are present but are rare and small (30-50µm). All are calcified, fractured and CL shows they contain brighter luminescing cements compared to the slightly duller non-ferroan cements that surround them. Clay and quartz content is less compared to the rest of the concretion due to an increase in carbonate content. However electrical microscopy shows kaolinite and quartz are still the main components of the micritic matrix that infills porosity between calcite grains (figure 4.8). B4-3H has isotopic values of δ¹³C -9.22‰, δ¹⁸O – 3.34‰ (table 4.2 and figure 4.6).

B4-2V is the vertical thin section sampled from the centre of the concretion, but near the top edge, not far from the contact with the organic rich mudstones. B4-2V is petrographically similar to B6 (figure 4.8). XRD shows that calcite content is significantly less compared to B4-1V and
B4-3H at 79%. Quartz content is higher at 12%, with kaolinite remaining the main clay mineral at 4-5% (table 4.1). Polarised microscopy shows a transition from a heavily recrystallised, fine grained dominated texture, to a more micritic dominated matrix containing floating foraminifera and sub-angular to angular calcite cement grains as the thin section traverses to the edge of the concretion (figure 4.8). CL shows the foraminifera contain brighter luminescing cements compared to the dull micritic matrix. The floating cement grains contain zoning cements with brighter luminescing cements near the grain edges with a duller luminescence in the centre of the grain. Electron microscopy shows the main component of the micritic matrix is coccolith fragments, micro-quartz cements and wisps of kaolinite (figure 4.8). B4-2V has isotopic values of δ\(^{13}\)C -2.21‰, δ\(^{18}\)O -5.23‰ (table 4.2 and figure 4.6).

B5 is located on the other side of the centre (B4) opposite B3 (figure 4.5). B5 contains coarser grained calcite cements compared to B4, similar in size and texture to B3. The bulk of cement grains are 1-15μm and are completely recrystallised (figure 4.8). Larger grains are present but do not exceed 50μm. Foraminifera are typically 50-80μm in diameter. CL shows they contain brighter luminescing cements compared to the duller non-ferroan cements that surround them. Like B1 and B2, electron microscopy shows a micritic rich matrix composed of coccolith fragments, kaolinite and quartz infilling porosity between calcite grains (figure 4.8). Peloids/pellets are present containing micrite, kaolinite, mixed layer I/S and micro quartz cements. Like the peloids/pellets in B3, the pellet/peloids in B5 are not surrounded by a recrystallised wall/shell. B5 has isotopic values of δ\(^{13}\)C –3.29‰, δ\(^{18}\)O -4.27‰ (table 4.2 and figure 4.6).

B6 is very similar to B1 and B4-2V. B6 is dominated by recrystallised calcite cements. Cement grains are sub-round to sub-angular and are mainly attached to one another. Some grains cross cut one another but this is rare. Grain sizes are 50-100μm (figure 4.8). Little biogenic material is present in B6, however foraminifera are common. All foraminifera are infilled with calcite and are larger than 100μm in diameter. Most have lost their shell walls to recrystallization, but some remain with their original shell walls with minor mictrisation. Electron microscopy shows a micritic rich matrix composed of coccolith fragments, kaolinite and quartz infills intergranular porosity between calcite grains (figure 4.8). B6 has isotopic values of δ\(^{13}\)C –1.74‰, δ\(^{18}\)O -5.52‰ (table 4.2 and figure 4.6).
4.3.5 Type 3

Figure 4.9. Diagram of a Type 3 concretion split into seven sections used for petrological and geochemical analysis. The transect begins at the edge and travels through the centre of the concretion to the other side at C6. A thin section was taken at the edge of each section. For each thin section, XRD and bulk stable isotope analysis was undertaken.

Three samples were extracted from the type 3 concretions; a core plug, a small rock sample from the edge of a concretion and a large rock sample, which was split into seven individual pieces for further analysis (figure 4.9).

In outcrop the type 3 concretions display sharp contacts with the surrounding organic rich mudstones and show no indication of erosion (figure 4.3). They have a lens like geometry and are discontinuous across at the same stratigraphic horizon. Sedimentary features are common. Cross trough stratification, sub-horizontal laminations, planar laminations and low and steep angle foresets are all present (figure 4.10).

Thin section analysis and XRD reveals (table 4.1) the core and small rock sample from the type 3 concretions are petrologically different compared to the type 2 concretions. Both contain an angular grain texture, however cement grain sizes in the type 3 concretions are larger (50-80µm) (figure 4.10). Like the type 2 concretions little biogenic material present. Preserved foraminifera tests are rare. They are recrystallised throughout. Foraminifera that are not recrystallised are fragmented and infilled with calcite (figure 4.10). Foraminifera shells are recrystallized with a
brown-grey calcite cement. Calcite cements surround the foraminifera and often attach to them. CL shows non ferroan calcite cement containing zoning. Cements are dull in the centre and brighten towards the edge of the grains. The matrix containing clay minerals and coccolith fragments remains black. The type 3 concretions are isotopically different compared to the organic rich mudstones and type 2 concretions. The type 3 concretions contain lighter $\delta^{18}O$ isotopic values and heavier $\delta^{13}C$ values compared to the type 2 concretions. M-C1: $\delta^{13}C$ -0.82‰, $\delta^{18}O$ -5.89‰. C1-RS: $\delta^{13}C$ -1.20‰, $\delta^{18}O$ -5.00‰ (table 4.2 and figure 4.6).

Like the type 2 concretions, a large junk from a type 3 concretion was extracted for analysis (figure 4.9). Sections C1-C6 and form a transect with C6 being nearest the centre of the concretion.

C1 and C2 are samples near the edge of the concretion and are identical under the microscope (figure 4.10). XRD shows calcite dominates the type 3 concretions (89.5, 91.8% respectively) (table 4.1). The calcite cement grains are larger compared to the type 2 concretions. In C1 and C2 the bulk of the calcite is anagular cements 50-100µm in size. Larger cement grains up to 120µm are present but rare. A micritic matrix is present between equant cement grains containing, coccolith fragments, kaolinite quartz and mixed layer I/S. SEM analysis reveals quartz cements are present within the micritic matrix as very fine grains (5-10µm) (figure 4.10). C1 has isotopic values of $\delta^{13}C$ -2.42‰, $\delta^{18}O$ -5.06‰ (table 4.2 and figure 4.7). C2 has isotopic values of $\delta^{13}C$ -2.10‰, $\delta^{18}O$ -5.03‰ (table 4.2 and figure 4.6).

C3 and C4 are samples nearer the centre of the concretion. They are petrologically similar to C1 and C2. XRD shows calcite dominates the samples, (91.2 and 87.2% respectively). Recrystallised calcite grains are 50-100µm like in C1 and C2. C3 and C4 differ from C1 and C2 because the varient distribution of the micritic matrix. The matrix is less evenly distributed between cement grains Nodules of matrix are present between some of the cement grains. The nodules of micrite are clay rich. Larger cement grains up to 120µm are present but rare. C3 has isotopic values of $\delta^{13}C$ -1.92‰, $\delta^{18}O$ -5.09‰ (table 4.2 and figure 4.7). C4 has isotopic values of $\delta^{13}C$ -2.14‰, $\delta^{18}O$ -5.07‰ (table 4.2 and figure 4.6).

C5 and C6 are near the centre of the concretion, which faces into the outcrop. They are petrologically identical to C1 and C2. XRD shows calcite dominates the samples, 89.1 and 88.3% respectively). Recrystallised calcite grains are 50-100µm like in C1 and C2. Larger cement grains up to 120µm are present but rare. C5 has isotopic values of $\delta^{13}C$ -1.82‰, $\delta^{18}O$ -5.00‰ (table 4.2 and figure 4.7). C6 has isotopic values of $\delta^{13}C$ -2.76‰, $\delta^{18}O$ -5.09‰ (table 4.2 and figure 4.6).
Figure 4.10. Type 3 concretion in thin section. A. Outcrop photograph of a type 3 concretion displaying sub-horizontal laminations (SHL) and cross trough laminations (CT). Note the none erosive contact with underlying and overlying organic-rich weakly laminated mustones. Rock hammer for scale. B. Thin section micrograph in plane polarised light of sample C1, displaying calcite cements (C). Grains are angular and 50-100µm in size. Some grains are up 120µm in size. The matrix (M) infills intergranular porosity. C. Thin section micrograph in plane polarised light of sample C4, displaying calcite cements (C). Cement grains are 50-100µm in size. Calcite content is higher in C4 (and C3) with a smaller quantity of the micritic matrix (red circle). Foraminifera (F) recrystallised and fragmented. D. Identical image to C but in CL. Calcite cements (C) contain non-ferroan, zoning cements. Cements display dull cements which gradually get brighter towards the edges of the grains. The micritic matrix remains black-brown (yellow circle). Some cements are much brighter (black arrows) suggesting additional phases of cementation.
have occurred. E. Thin section micrograph in plane polarised light of sample C6, displaying calcite cements (C). Cement grains are angular and 50-100µm in size. They are petrologically similar to C1 and C2. The micritic matrix infills intergranular porosity between cements grains. F. SEM-BSE micrograph of C1 (2780013) displaying angular, equant calcite cements (C), with quartz (Q), kaolinite (K) and coccolith fragments (CC) infilling intergranular porosity between the calcite cements.

4.3.6 Type 4

Three outcrop samples were extracted from the type 4 concretions. Two small samples were extracted from outcrop, including a small horizontal core. A third, larger segment was also extracted from the outcrop which was split into six segments for further petrological and gemochemical analysis.

In outcrop the type 4 concretions are continuous and extend (>1km) throughout the entire outcrop like the type 1 concretions. Their geometry varies. Type 4 concretions are mostly a thin continuous bed of limestone approximately 10cm thick but ‘pulse’ in localised areas to a thickness of ~30cm. These pulses are elongated, elliptical in shape similar to the Type 3 concretions; however they are connected by a thin strand of limestone that runs continuously throughout the outcrop (figure 4.3). The type 4 concretions, like the type 3 concretions display sharp contacts above and below the surrounding organic rich mudstones (figure 4.11). They show no evidence of erosion and contain cross trough stratification, sub horizontal laminations, low and steep angle foresets. Like the type 1 concretions they are directly above a substantial bentonite bed, which also traverses the entire outcrop (>1km) (figure 4.11).

Thin section analysis shows that the type 4 concretions contain sub-angular carbonate cements ranging in size from 60-80µm in size. Benthic and planktonic foraminifera are common (figure 4.11). Inocerimid bivalves, echinoid fragments and calcispheres are present but rare. Calcified radiolarians are commonly seen in thin section. All biota have been preserved to a degree by the infilling and/or replacement of calcite, although most biota are fragmented and recrystallised. Equant carbonate cements overprint the original composition leaving the remnants of the organic rich mudstones. No pyrite is measured in XRD (table 4.1) and is not observed under SEM. CL reveals calcite is non-ferroan and a
Figure 4.11. Concretion Type 4 in thin section. A. Photograph of a type 4 concretion (GPS unit sitting on top and for scale). A thin concretion bed traverses the outcrop with pulsating areas of carbonate. Sub horizontal laminations (SHL) and cross trough bedding (CTB) are common (black lines). B. Thin section micrograph in plane polarised light of sample D1, displaying calcite cements (C). Grains are angular and 60-80µm in size. Foraminifera (F) are intact and infilled with calcite cement. Larger benthic foraminifera are fragmented (FF). A micritic matrix (M) containing coccolith fragments, kaolinite, quartz and mixed layer I/S infills inter-granular porosity between calcite cements. C. Thin section micrograph in plane polarised light of sample D3, displaying calcite cements (C). Grains are angular and 60-80µm in size. Foraminifers (F) are intact and infilled with calcite cement. Radiolarians (R) are calcified and sometimes fragmented. A micritic matrix (M) containing coccolith fragments, kaolinite, quartz and
mixed layer I/S infills inter-granular porosity between calcite cements. D. Thin section micrograph in CL of sample D3, displaying non-ferroan, zoned calcite cements (C). Radiolarians (R) contain brighter non-ferroan zoned cements with brighter fluorescing edges. E. SEM-BSE micrograph of D1 displaying the equant calcite cement grains (C). Quartz (Q) is commonly seen within the micritic matrix and infilling micron-sized intra-granular pores. Kaolinite (K) is also observed between calcite cement grains. F. SEM-BSE micrograph of D1 displaying equant calcite cement grains (C), micro-quartz (Q), kaolinite (K) and mixed layer I/S (I/S) within the micritic matrix that infills inter-granular porosity between calcite cement grains.

High quantity of the calcite is precipitated in one phase. Some foraminifera chambers and the cements surrounding them display zonations.

Electron microscopy shows a micritic matrix (3-7µm) is present between the equant cement grains. Coccolith fragments are main component of the matrix along with wisps of mixed-layer I/S and kaolinite. Clay and organic matter are also present albeit in small quantities. Organic matter is sporadic and is present as small flakes (~5-6µm). The type 4 concretions contain the lightest $\delta^{18}$O isotopic values and heaviest $\delta^{13}$C values compared to the other concretions. D1 has isotopic values of $\delta^{13}$C -1.05‰, $\delta^{18}$O –5.46‰ D2 $\delta^{13}$C –1.34‰, $\delta^{18}$O -5.54‰ D3 $\delta^{13}$C -1.17‰, $\delta^{18}$O -5.56 (table 4.2 and figure 4.6).
4.4 Interpretation and Discussion

4.4.1 Organic-rich weakly laminated mudstones

Extensive and detailed petrographic, mineralogical and geochemical analysis of the organic-rich weakly laminated mudstones and carbonate concretions within the Upper Cretaceous Eagle Ford Fmn, suggest these lithofacies/structures were influenced to an extent, by diagenesis. Similar finding are observed in the Natih-B formation, Oxford Clay and Kimmeridge Clay Formaiton (Al Balushi, 2013, Friedman, 1964, Taylor, 2010). The organic-rich mudstones and the four concretions types vary in terms of composition, compaction and influence of diagenesis.

The organic-rich weakly laminated mudstones are highly compacted, fissile (only in outcrop) and laminated. Carbonate is the main component of the mudstones, with coccolith fragments constituting the bulk of the matrix along with clay minerals. Sparry calcite cements infilling uncompacted planktonic foraminifera tests are the only pervasive carbonate cements that look to be precipitated via diagenetic processes. Pervasive authigenic silicate cements present in the matrix are interpreted to be late diagenetic processes that have occurred at depth.

The texture and composition of the organic-rich weakly laminated mudstones comprising of coccolith fragments, planktonic foraminifera and inoceramid bivalves suggests that these units were deposited in an open-marine, basinal environment (Arthur and Sageman, 2004, Al Balushi et al., 2013, Lowery et al., 2014, Corbett and Watkins, 2013). The lack of benthic species in this lithofacies, the absence of burrowing and the nature of calcite cements precipitated indicate the depositional setting was likely to be oxygen depleted (Wignall, 1994, Pederson and Calvert, 1990, Taylor and Macquaker, 2014, Macquaker et al., 2014). Intact sub-millimetre to millimetre scale, planar laminae suggest the organic rich mudstones were deposited below storm wave base. However, some laminae are truncated or contain wavy ripples suggesting some bottom water currents reworked the finer grained sediments. Since truncated laminae are rare, we infer bottom water currents were episodal and occurred rarely (Schieber et al., 2010, Bohacs, 1998, Macquaker and Gawthorpe, 1993, Macquaker and Adams, 2003).

In core, the black to dark brown colour of the organic-rich weakly laminated mudstones is caused by the organic carbon content, the presence of clay minerals and pyrite, although the latter constitutes a small (<6.5%) proportion of the total composition.
High organic carbon content in the Lower Eagle Ford Fmn is thought to be mainly driven by depositional environments that were ideal for organic carbon preservation, i.e. anoxia, and a stagnant water column. (Liro et al., 1994, Corbett and Watkins, 2013, Lowery et al., 2014). Evidence of anoxic deposition conditions are the presence of inoceramid bivalves, the lack of benthic species and the lack of fauna diversity, with planktonic foraminifera and coccolith debris the only other species present in the organic-rich lithofacies (Corbett and Watkins, 2013, Lowery et al., 2014).

Brighter luminescing, non-ferroan, zoned cements within foraminifera associated with pyrite, are all indications of early diagenetic, microbial-mediated redox reactions taking place in a suboxic to anoxic setting (Curtis and Spears, 1968, Curtis, 1977, Curtis, 1995, Presley and Kaplan, 1968, Coleman and Raiswell, 1995). The zonation of calcite cements implies that there were variations in pore water chemistry during burial. Sulphate reduction is one well known process that occurs in oxygen depleted sediments just below the sediment water interface (up to 30cm depth) (Curtis and Spears, 1968, Curtis, 1977, Curtis, 1995, Presley and Kaplan, 1968, Moses and Herman, 1991). Sulphate reduction removes sulphate from the pore waters by liberating hydrogen sulphide and creating pyrite. Bicarbonate is sequestered into the surrounding pore waters allowing the early precipitation of non-ferroan calcite cements. Similar cements are observed in the Kimmeridge Clay formation, UK, Natih B formation, Oman and Lower Jurassic Cleveland Ironstone, UK (Al Balushi et al., 2013, Macquaker et al., 2014, Taylor, 2010).

Bulk stable \( \delta^{13}C \) isotopes suggest that the carbonate within the organic-rich weakly laminated mudstones was precipitated from normal-marine, oxic pore waters with little indication of diagenetic processes taking place (figure 4.7) (Irwin, 1977, Singleton et al., 2002). This could be due to the bulk sampling technique, although the main cause is likely that carbonate is mainly observed as coccolith fragments sourced from seawater, buffering the effects of minor organogenesisis during burial. Bulk stable \( \delta^{18}O \) isotopes suggest carbonate was precipitated at temperatures of 50-60°C (Irwin, 1977, Singleton et al., 2002, Pepper and Corvit, 1995, Friedman and O'Neill, 1977). Average global Late Cretaceous sea surface temperatures are thought to be ~30°C, implying bulk of carbonate was precipitated at depth or an input of meteoric water has occurred (Weimer, 1990, Scott, 1993, Schlanger and Jenkyns, 1976, Martin et al., 2012, Elder and Kirkland, 1994, Corbett and Watkins, 2013, Singleton et al., 2002, Irwin, 1977, Arthur and Anderson, 1983, Anderson and Arthur, 1983). The ecology present in thin section strongly implies that the Eagle Ford Fmn was deposited in an open marine system (Lowery et al., 2014, Corbett and Watkins, 2013, Donovan et al., 2012). Therefore the input of meteorological water is
highly unlikely. Scanning electron microscopy reveals marine derived carbonate as coccolith debris are the main carbonate component in the organic-rich weakly laminated mudstones. These fragments commonly display a euhedral-like shape, indicating they have undergone mild recrystallisation (figure 4.5) – likely at depth due to the negative $\delta^{18}$O values indicating pore fluid temperatures of 50-60°C (Singleton et al., 2002, Irwin, 1977, Friedman and O'Neill, 1977). Sulphate reducing bacteria producing sparry calcite cements infilling foraminifera are interpreted to have had little effect on the bulk isotopic compositions of carbonate in the organic-rich weakly laminated mudstones (Singleton et al., 2002, Friedman, 1964, Curtis, 1977).

Kaolinite is commonly observed co-filling (with calcite) and filling foraminifer chambers and is interpreted to have precipitated early during diagenesis, in normal marine or modified pore waters. The presence of authigenic clay minerals, in particular kaolinite, further suggest organic matter degradation has taken place to a certain degree (Al Balushi, 2013, Macquaker et al., 2014, Macquaker and Gawthorpe, 1993, Taylor and Macquaker, 2014, Yamaguchi et al., 2010, Silva and Duarte, 2015, Taylor, 2010, Presley and Kaplan, 1968, Coleman and Raiswell, 1995, Bottrell and Raiswell R., 1989). The degradation of organic matter through sulphate reduction, and the thermo-chemical decay of organic matter later in burial are all associated with organic acids within the pore waters (Barcelona, 1980, Taylor and Macquaker, 2011, Taylor and Macquaker, 2014, Macquaker et al., 2014, Macquaker et al., 1997). Organic acids, such as carboxylic acid, are likely to be responsible for Al mobilisation as they dissolve Al-rich amorphous material providing the components to produce authigenic kaolinite (Barcelona, 1980, Macquaker et al., 2014, Burton et al., 1987). Organic acids associated with OM degradation were likely to be dissolving biogenic silicate (radiolarians, opal CT) at an early stage of burial prior to compaction (Barcelona, 1980, Schieber et al., 2000, Thyberg et al., 2010, Macquaker et al., 2014). The precipitation of authigenic quartz is a late diagenetic process. At higher magnifications quartz is seen infilling pore space between coccolith fragments and as small grains attached to calcite cements (Thyberg and Jahren, 2011, Thyberg et al., 2010, Al Balushi, 2013, Macquaker et al., 2014, Taylor and Macquaker, 2014). The release of Si from smectite to illite reactions is the likely source of free Si during late diagenesis at temperatures of $>$90 where quartz cements can precipitate in the organic-rich weakly laminated mudstones (Bethke et al., 1986, Freed and Peacor, 1989, Nadeau et al., 1985, Niu et al., 2000, Peltonen et al., 2009, Thyberg and Jahren, 2011). Authigenic quartz cements can act as a stiffening agent reinforcing and further strengthening the rock composition (Thyberg and Jahren, 2011, Thyberg et al., 2010).
The organic-rich weakly laminated mudstones are heavily compacted compared to the concretions. Organic-rich weakly laminated mudstones surrounding the type 2 concretions display differential compaction in core and outcrop (figure 4.3 and 4.13), indicating the concretions were present before any significant compaction during burial (Coleman, 1993, Cade and Gluyas, 1992).

![Image](image_url)  
*Figure 4.12. A. The edge of a type 2 concretion in core displaying differential compaction (red lines) around the concretion. Notice how laminae tend not to thin but just differentiate around the concretion. B. Laminations bend around a type 2 concretion in core.*

Laminations are commonly deformed and bend around the concretions (figure 4.12). Cade and Gluyas, 1992, developed a constrained model based on marine mudstones in the North Sea to extrapolate the de-compaction value of mudstones suggesting that a clay dominated (>80%) mudstone loses between 30-35% of its total porosity through compaction. By multiplying the thickness of a particular bed or lamination by 3.226, we can calculate the original thickness of the sediment deposited at the sediment water interface. Secondly, an approximation of how much sediment was deposited compared to the rate of carbonate precipitation by counting the laminations surrounding the apexes of the concretions (Cade and Gluyas, 1992, Sheldon and Retallack, 2001). In the case using the concretion in figure 4.12, average laminae thickness is 1.9mm giving an average de-compaction thickness of ~6.13mm. 14 individual laminations were observed displaying differential compaction surrounding the edge of a concretion in core (figure 4.12). This equates to 85.13mm of sedimentation during the growth of this particular concretion. Type 2 concretions in outcrop are ~250mm in height, which suggests sedimentation rates were
not substantial enough to fully bury the type 2 concretions as they were forming. This implies the type 2 concretions were likely to be present on the seafloor during deposition. The author does exercise caution, as Cade and Gluyas, 1992 explicitly state the mudstone used to devise such as model is clay-rich (>80%). The Lower Eagle Ford Fmn in this study is highly calcareous (>40%) and is likely to behave differently during compaction (figure 4.4). Also in core, a lack of spatial resolution makes it impossible to access how big the concretion was in regards to the differential laminations around it.

Arthur et al 2004, discuss, for organic matter enrichment in the Western Interior Seaway, there was a decrease in sedimentation rates, but still enough was deposited to preserve organic matter. They also state sedimentation rates are likely to decrease overall in an east to west direction, which is supported by the presence of more calcareous mudstone observed in the Eagle Ford Fmn in west Texas, compared to the more siliceous material in the east (Arthur and Sageman, 2004, Donovan et al., 2012, Kauffman, 1984). Egger et al 2008, however, state that for high TOC content, there must have been relatively high sedimentation rates in the Western Interior Seaway. They show sedimentation rates during the age equivalent Rhenodanubian Group in the Eastern Alps, Germany, had an average 25mm/kyr$^{-1}$ sedimentation rate, with a maximum of 60mm/kyr$^{-1}$ (Egger and Schwerd, 2008). These sedimentation rates are very low (Egger and Schwerd, 2008, Kauffman, 1984, Kauffman and Sageman, 1990, Lock et al., 2001, Arthur and Sageman, 2004, Brigaud et al., 2008, Monroe and Wicander, 2009). Modern deep sea fans receive 100-1000mm/kyr$^{-1}$ (Egger and Schwerd, 2008). If siliceous sedimentation rates are not enough to preserve organic carbon, carbonate production at the sediment water interface could have been a factor decreasing exposure time on the sea floor (Egger and Schwerd, 2008, Kauffman, 1984, Kauffman and Sageman, 1990, Arthur and Sageman, 2004, van Buchem et al., 2005). The organic-rich weakly laminated mudstones are interpreted to represent moderate to high primary production, with a significant oxygen minimum zone present in the water column. They also represent the processes of episodic, fine grained sediment supply and burial during transgression, thus an increase in accommodation, which allowed for the preservation of organic matter (Wignall, 1994, Tyson, 2005, Trevino, 1988, Arthur and Sageman, 2004). The high TOC values present in the organic rich mudstones suggest organic particulates were buried relatively quickly, or were preserved due to a lack of degradation via oxic respiration. TOC values of 6-8%, the lack of biogenic diversity with just the presence of planktonic foraminifera and inoceramid bivalves points towards an oxygen depleted environment at the sediment water interface (Tyson, 2005, Donovan et al., 2012, Silva and Duarte, 2015).
4.4.2 Concretions

In core and outcrop the light grey to grey colour of all the types of concretion (figure 4.2 and 4.12) is caused by the volume of calcite cements and the lack of organic matter compared to the organic-rich weakly laminated mudstones (figures 4.7, 4.8, 4.9, 4.10). Bacterial-mediated iron and sulphate reduction is interpreted to have precipitated authigenic non-ferroan, zoned, equant calcite cements in all the concretions. Zonations within calcite cements imply that there were variations in pore water chemistry during burial (Al Balushi et al., 2013, Macquaker et al., 1997, Macquaker et al., 2014, Taylor and Macquaker, 2011, Presley and Kaplan, 1968). In thin section extensive pervasive carbonate cements have replaced and recrystallised most of original matrix and foraminifera shells. A lack of fauna identity, along with recrystallised cement grains suggests a second phase of carbonate precipitation or carbonate mobilisation during later burial. The type 2 concretions are interpreted to have recrystallised relatively early compared to the other concretions (figure 4.6).

Bulk stable isotopic compositions of carbonate (Table 4.2 and figure 4.6) along with the precipitation of non-ferroan, zoned, equant calcite crystals suggests a mixture of marine sourced and diagenetically sourced carbonate in concretions 1, 3, and 4. Similar findings were recorded in the Hanford Site, Pasco Basin, Washington, USA (Irwin, 1977, Singleton et al., 2002, Anderson and Arthur, 1983, Arthur and Anderson, 1983). δ13C compared to the organic-rich weakly laminated mudstones are depleted (Type 1: average values δ13C -1.54‰. Type 3: average values δ13C -1.54‰, Type 4: average values δ13C -1.20‰), indicating there was an input of depleted carbon into the sediments during deposition. The type 2 concretions are heavily depleted in δ13C (average δ13C -6.02‰) suggesting extensive carbonate precipitation via microbial induced redox reactions. Isotopically lighter carbon is produced by the degradation of organic matter via iron and sulphate reduction (Presley and Kaplan, 1968, Curtis, 1977, Curtis, 1995, Curtis and Spears, 1968). Aerobic respiration of organic matter in the water column and/or sediment water interface is also a possible cause for degraded organic material due low TOC values (El Albani et al., 2001, Silva and Duarte, 2015, Tyson, 2005, Pederson and Calvert, 1990). A significant bulk of the carbonate is marine sourced and is observed under SEM as coccolith fragments between equant cement grains, which comprise the bulk of all the concretion types. Only in the centre of type 2 concretions is the absence of coccolith fragments and a micritic matrix. A mixture of recrystallised marine derived and diagenetic carbonate comprises the bulk mineral composition of the concretions. Diagenetic carbonate is produced through bacterial mediated iron and sulphate

The $\delta^{18}O$ values obtained from the concretions indicate elevated pore fluid temperatures compared to Late-Cretaceous seawater (Anderson and Arthur, 1983, Arthur and Anderson, 1983). Heavier $\delta^{18}O$ values in the type 1 concretions (figure 4.6) compared to the organic-rich weakly laminated mudstones suggest carbonate was recrystallised at depth where pore-fluid temperatures were approximately 40°C, the type 2 concretions 35°C, type 3: 35-40°C and the type 4: 45-50°C (Anderson and Arthur, 1983, Arthur and Anderson, 1983). Temperatures estimated through the $\delta^{18}O$ compositions are difficult to distinguish since the cements and the original shell material within the concretions are diagenetically modified and recrystallised. No evidence is present to link the $\delta^{18}O$ values to the input of meteoric waters or sub-aerial exposure causing negative $\delta^{18}O$ values. Positive $\delta^{18}O$ values ~ +5‰ are indicative of meteoric water input (Anderson and Arthur, 1983, Friedman and O'Neill, 1977, Kim and O'Neill, 1997, Al Balushi et al., 2013, Marshall and Pirrie, 2013, Berner and Faber, 1996). The presence of some foraminifera and inoceramid bivalves in the organic-rich weakly laminated mudstones clearly indicates the Eagle Ford Fmn was deposited in a normal marine environment where meteoric water input and/or sub aerial exposure is near impossible (Anderson and Arthur, 1983, Friedman and O'Neill, 1977, Kim and O'Neill, 1997, Al Balushi et al., 2013, Marshall and Pirrie, 2013, Berner and Faber, 1996). Regardless, seawater temperatures during the Late-Cretaceous were relatively warm with paleotemperatures estimated in the Western Interior Seaway during the Cenomanian-Turonian ~30°C (Anderson and Arthur, 1983, Friedman and O'Neill, 1977, Kim and O'Neill, 1997). Since the $\delta^{18}O$ are relatively light the concretions are interpreted to have experienced recrystallisation at depth where temperatures are excess of 35°C (Friedman, 1964, Friedman and O'Neill, 1977, Singleton et al., 2002).

Despite similar mineralogy and textures, diagenetic pathways and thus isotopic compositions (bar the type 2 concretions), the concretions are interpreted to have differing mechanisms that created each type. Interpretations of the mechanisms that formed them are further based on observations in outcrop, such as their size, shape, distribution and surrounding lithology’s.

4.4.2.1 Interpretation of the Type 1 Concretions

The type 1 concretions are extensive in outcrop (>1km) and are 20-30cm thick suggesting a fundamental change to depositional environment allowing for carbonate to precipitate at the sediment water interface (figure 4.3). Similar features have been observed in the Natih-B
formation in Oman, The Upper Bone Spring Limestone, and the Kimmeridge Clay formation in the UK (Al Balushi et al., 2013, Astin and Scotchman, 1988, Asmus, 2012) The type 1 concretions are continuous throughout the Eagle Ford Fmn and are interpreted to be deposited on a basinal scale (Donovan et al., 2012, Liro et al., 1994, Dawson, 1997). Sufficient exposure of organic material at the sediment water interface can cause extensive degradation of organic matter via aerobic or anaerobic metabolism (Curtis, 1977, Curtis, 1995, Tyson, 2005). Sediments that are slowly buried allow for prolonged bacterially mediated oxidation of the organic material, significantly reducing TOC and precipitating bicarbonate (Curtis, 1977, Al Balushi et al., 2013, Bathurst, 1974, Brigaud et al., 2009, Friedman, 1964). Rising sea levels and subsequent sea level high stands are interpreted to be the cause of reduced sediment input allowing the degradation of organic matter at the sediment water interface with the type 1 concretions representing the additional carbonate precipitated throughout the basin (Bohacs, 1998, Tucker and Wright, 1990, Al Balushi et al., 2013, Aplin, 2000, Bathurst, 1974). The presence of a significant bentonite bed immediately below the type 1 concretions (figure 4.3) is thought to have an impact on the depositional environment that deposited the material immediately above it. Volcanic activity is the likely source of bentonite into the Western Interior Seaway (Elder, 1988). Volcanic ash falling onto the sea surface has a detrimental effect on primary productivity in the surface waters. Volcanic ash contains high levels of iron and other nutrients vital to primary productivity (Elder, 1988, Tyson, 2005, Pederson and Calvert, 1990). A large, sudden increase of iron into an open marine environment causes primary productivity plumes in the surface waters (Silva and Duarte, 2015, Elder, 1988, Elder and Kirkland, 1994). With higher levels of phytoplankton in the surface waters, trophic level predators, which make their carbonate shells with carbonate, flourish. These species die and fall to the sea bed aiding in the deposition of a substantial, 30cm thick carbonate rich interval across the Eagle Ford Fmn.

Overall, a number of factors are interpreted to have caused the formation of the type 1 concretions. A fifth-order sea level highstand reduced siciliclastic sediment supply, allowing for carbonate precipitation via microbially induced redox reactions and the degradation of organic matter (Liro et al., 1994, Bohacs, 1998, Dawson, 1997, Schlager, 2005). Volcanic activity from the North American interior delivered a layer of volcanic ash to the region (Elder, 1988, Elder and Kirkland, 1994). The sudden input of iron created primary productivity plumes, which created an increase in the population of trophic level predators. With extra skeletal material accumulating on the seabed, sediment starvation due to a sea-level high stand, carbonate was precipitated throughout the entire basin.
4.4.2.2 Interpretation of the Type 4 Concretions

The type 4 concretions are similar in texture and composition compared to the type 1 concretions (Table 4.1 and figure 4.10). Like the type 1 concretions the type 4 concretions traverse the >1km outcrop and have a bentonite bed directly beneath them. However the type 4 concretions display ripple like laminae and cross laminations. Sedimentary structures indicate they were present on the seafloor and formed syn-deposition where bottom water currents carrying fine grained sediment could form the sedimentary structures we observe in outcrop (Al Balushi et al., 2013, Asmus, 2012, Bathurst, 1974, Cook and Mullins, 1983, Droste and van Steenwinkel, 2004, Flugel, 2010).

Calcified radiolarians are a common feature in concretion types 1 and 4, indicating high primary productivity levels in the photic zone and high concentrations of CO$_2$ in the ocean waters due to the destruction of their silica shells during deposition (Schieber et al., 2000, Thyberg et al., 2010) (Bathurst, 1974, Schlager, 2005, Scott, 1993, van Buchem et al., 2005). The presence of calcified radiolarians in thin section and bentonite beds directly beneath the concretions suggests a significant quantity of carbonate was marine-derived via photic zone predators, during a productivity bloom caused by volcanic input (Elder, 1988, Elder and Kirkland, 1994, Corbett and Watkins, 2013, Donovan et al., 2012, Lowery et al., 2014, Frebourg, 2015). Unlike the type 1 concretions, reduced sedimentation rates were not a factor with sediment clearly being supplied to the seafloor due to the sedimentary structures observed in the type 4 concretions. With an increased supply of marine derived carbonate supplied from the photic zone via skeletal material, but with similar sediment input as the organic-rich weakly laminated mudstones, a thinner band of carbonate is observed traversing the outcrops.

4.4.2.3 Interpretation of the Type 3 Concretions

The type 3 concretions do not contain calcified radiolarians in thin section and do not have an underlying bentonite bed (figure 4.11). They are lenticular or elliptical in shape and are discontinuous in outcrop, no larger than 10cm thick, but vary in length. Some concretions are <50cm while others can be >1.5m long (figure 4.3). Like the type 4 concretions they contain ripple laminae, cross trough stratification and ripple beds on top indicating they were formed syn-deposition and present on the seafloor. We infer the mechanism that produced the type 3 concretions was sea-level variation, likely fifth-order eustatic sea-level rise that reduced sediment supply to the basin (Corbett and Watkins, 2013, Lowery et al., 2014, Kauffman, 1984, Arthur and Sageman, 2004, Elder and Kirkland, 1994, Longman et al., 1998). Longman et al., 1998, and
Arthur and Sageman, 2004, observe regular, lateral cyclic alterations of organic-rich mudstone and limestone beds/concretions, on a sub-metre (concretion) to >1km in Late-Cretaceous mudstones throughout the Western Interior Seaway and interpret these to be fifth-order eustatic sea level variations. Dawson 1997, also highlights the cyclic behaviour of organic-rich mudstone and limestone beds in the Lower Eagle Ford Fmm. Here he suggested some of the possible mechanisms that could have produced such structures such as variations in sea level, sediment input and primary production. However, Dawson 1997 was merely a petrographic comparison of the mudstones and limestones and does not divulge into any detail how the structures may have been formed.

Like the type 1 concretions, fifth-order eustatic sea level variations, in particular transgression and subsequent high stands are interpreted to have reduced sediment supply to the basin, causing sediment starvation at the sediment water interface during deposition of the type 3 concretions. Sporadic sedimentation left certain areas of the seafloor exposed allowing for microbially-mediated sulphate reducing bacteria to oxidise organic matter and precipitate carbonate. Bottom water currents re-distributed sediment creating the sedimentary structures observed in outcrop but allowing the formation of lenticular, discontinuous concretions across a stratigraphic horizon. Periods of low sedimentation rates that allow the precipitation of CaCO₃ are observed in the Greenhorn Fmn, USA (Elder and Kirkland, 1994, Arthur and Sageman, 2004). Reduced sedimentation rates leads to the oxidation of organic matter as it is exposed for longer periods on the sea floor to reducing agents (Tyson, 2005, Wignall, 1994, Pederson and Calvert, 1990, Arthur and Sageman, 2004). Sea level rise, causing a more distal basin environment, reduces sediment input from the interior reaching the basin (Aplin and Macquaker, 2011, Bohacs, 1998). Within the same horizon, areas that display organic-rich weakly laminated mudstone were supplied sufficiently with siliciclastic sediment which restricted microbial redox reactions.

Elder et al 1994 discuss how siliciclastic sedimentation is likely to be restricted to the west of the Western Interior Seaway with tectonic and eustatic sea-level fluctuations the drivers of sedimentation rates. However, others suggest these mechanisms may be overprinted by volcanic activity (Elder, 1988, Elder and Kirkland, 1994, Stanley, 1999, Monroe and Wicander, 2009). Many authors have stated that primary productivity rates in the Western Interior Seaway were stable during the Late Cretaceous (Elder, 1988, Elder and Kirkland, 1994, Kauffman, 1984, Kauffman and Sageman, 1990, Arthur and Sageman, 2004). However, Frebourg 2015 concludes a bloom in surface water productivity due to volcanic ash input creates additional sedimentation.
at the seafloor in the form of skeletal debris from photic level predators, which creates the carbonate rich concretions. The of this hypothesis is agreeable, however the isotopic compositions of the carbonate present in the type 1, 3 and 4 concretions indicates a significant quantity of carbonate has been produced and/or modified through. With reduced TOC values compared to the surrounding organic-rich weakly laminated mudstones, we infer sedimentation was reduced, increasing exposure times at the sediment water interface to allow the degradation of organic matter (Tyson, 2005, Pederson and Calvert, 1990, El Albani et al., 2001).

The type 1, 3 and 4 concretions contain a similar micritic matrix between the equant cements which is also present within the organic-rich weakly laminated mudstones. The matrix comprises of mixed layer I/S, smectite, illite, kaolinite along with coccolith fragments. Smectite is a fine grained terrestrial component that is still able to be transported to distal environments (Bethke et al., 1986, Boles and Franks, 1979, Freed and Peacor, 1989, Leo Lynch, 1997, Nadeau et al., 1985, Niu et al., 2000). Smectite is a primary depositional feature and shows clastic sedimentation still occurred throughout the Western Interior Seaway, despite an interpreted decrease in sediment input in the type 1 and type 3 concretions. There is some uncertainty whether the type 4 concretions experienced sediment starvation and were formed by extra sedimentation of biogenic carbonate. The presence of the coccolith-rich matrix in these types of concretions has two implications; 1) They were likely to be originally organic rich mudstones, but have been modified due to the early precipitation of carbonate cements that have overprinted the original composition. 2) They were deposited in the same environment as the organic rich mudstones, but with a decreased sediment supply, allowing the precipitation of carbonate at the sediment water interface via microbial-induced redox reactions (Curtis, 1977, Curtis, 1995, Macquaker et al., 1997, Coleman, 1993, Coleman and Raiswell, 1993).

**4.4.2.4 Interpretation of the Type 2 Concretions**

The type 2 concretions contain different textures and compositions and have little resemblance to the other concretion types. The type 2 concretions are thought to be purely diagenetic features due to their texture, composition, their location and distribution within the organic-rich weakly laminated mudstones in outcrop, and their isotopic compositions (Coleman, 1985, Coleman, 1993, Coleman and Raiswell, 1995, Astin and Scotchman, 1988, Scotchman, 1991, Scotchman, 1989). Differential compaction of the organic-rich weakly laminated mudstones is present around the type 2 concretions with laminations bending around the “football” like structures. This is also evident in core (figure.4.12). We infer 80-90% of the total volume of concretions were in place
within the organic-rich weakly laminated mudstones before any significant compaction had taken place. The outer edges of the concretion contain relatively higher amounts of clay minerals and contain differing isotopic compositions suggesting the concretion edges were formed through the recrystallisation of the surrounding organic-rich weakly laminated mudstones (figure 4.9).

Due to the elliptical-like shape of the type 2 concretions and isotopic compositions, the centre is interpreted to be the origin, with the carbonate in the centre precipitated first. As carbonate precipitated the concretions continued to grow outwards. The very centre (B4-3H), of the concretion contains depleted $\delta^{13}$C (-9.22‰) and enriched $\delta^{18}$O (-3.34‰) values. The relatively isotopically light (depleted) $\delta^{13}$C values in the centre suggest organogenesis has taken place during early burial creating the initial carbonate centre. The very fine cement grains suggest carbonate has precipitated rapidly (Astin and Scotchman, 1988, Scotchman, 1989, Scotchman et al., 2000, Coleman, 1993, Coleman and Raiswell, 1993). The $\delta^{18}$O values suggest initial carbonate precipitation occurred at approximately 35°C (Anderson and Arthur, 1983, Arthur and Anderson, 1983, Singleton et al., 2002, Irwin, 1977). As the concretion continued to grow throughout burial, temperatures increased and organogenesis became less of a factor (Coleman, 1993, Coleman and Raiswell, 1995, Coleman and Raiswell, 1993, Marshall and Pirrie, 2013). This is reflected in the isotopic compositions and larger cement grains precipitated suggesting carbonate precipitation slowed (Coleman, 1993, Berner, 1968). The surrounding carbonate around the centre of the concretion (B3 and B5, (Figure 4.8), also contains depleted $\delta^{13}$C values and enriched $\delta^{18}$O values, but $\delta^{13}$C values are heavier (-8.61‰ and -3.29, B3 and B5 respectively) and $\delta^{18}$O values are lighter (-3.34‰ and -4.27, B3 and B5 respectively) compared to the very centre of the concretion. Carbonate surrounding the centre is interpreted to be precipitated during later diagenesis where fluid temperatures were higher due to burial (Berner, 1968, Astin, 1986). The edges of the concretion (B1, B2, B6 and B4-2V)(figure 4.6), contain contrasting isotopic values compared to the centre of the concretion. The compositions are similar to the type 1 and type 3 concretions (B1- $\delta^{13}$C -2.14, $\delta^{18}$O -5.02; B2- $\delta^{13}$C -1.95, $\delta^{18}$O -4.51; B6- $\delta^{13}$C -1.74, $\delta^{18}$O -5.52; B4-2V- $\delta^{13}$C-2.21, $\delta^{18}$O -5.23). Here the $\delta^{18}$O isotopic signatures suggest carbonate was precipitated at depth compared to the centre of the concretions due to their converted temperature factors (Singleton et al., 2002, Anderson and Arthur, 1983, Arthur and Anderson, 1983). However the $\delta^{13}$C values indicate carbonate precipitated at depth obtains an overall marine signature, which may have been modified through the recrystallisation of the surrounding organic-rich weakly laminated mudstones (figure 4.8).
When the centre of the type 2 concretion was analysed there was no indication of a core like structure, such as a piece of organic material or something obvious like shell material where carbonate is likely to precipitate (Astin, 1986, Astin and Scotchman, 1988, Pearson et al., 2005). Many authors (Braissant et al., 2007, Astin and Scotchman, 1988, Scotchman et al., 2000, Macquaker et al., 2014, Curtis, 1977) discuss how sulphate-reducing bacteria are key players in the precipitation of calcium carbonate through consuming organic acids (organic material). Braissant et al., 2007, demonstrate how sulphate-reducing bacteria produce exopolymeric substances (EPS), which colonise local areas of the lithology influencing the morphology, mineralogy and precipitation of carbonate minerals. Local communities of EPS creating lithifying microbial mats are interpreted to have precipitated the type 2 concretions within the surrounding organic-rich weakly laminated mudstones. The influence of a bentonite bed directly underlying the type 2 concretions and organic-rich weakly laminated mudstones is unknown. One suggestion is the type 1 and type 4 concretions are a continuation of the type two concretions where enough carbonate has precipitated across the entire stratigraphic horizon joining the type 2 concretion together. However the type 2 concretions have no obvious or apparent link to these features due to their isotopic values, texture and morphology.

Iron content within concretions increases with heavier $\delta^{13}$C and lighter $\delta^{18}$O reflecting the lessening influence of the sulphate reduction zone (Macquaker et al., 1997, Coleman, 1985, Coleman and Raiswell, 1995, Astin and Scotchman, 1988, Scotchman, 1991). First generation calcite cements precipitated as a by-product of sulphate reduction are non-ferroan, while the outer later cements blend into a more ferroan calcite (Scotchman, 1991). This process reflects the burial of sediments deeper into the sub-surface where they leave the realms of sulphur reduction and enter other diagenetic zones.

Other elements such as manganese, sulphur and magnesium are also helpful markers of a concretions/limestone origin. Mn and Fe are closely related in diagenetic concretions, with the ratio (Mn/Fe) between the two a good indicator of which diagenetic processes have taken place (Astin and Scotchman, 1988, Scotchman, 1991, Braissant et al., 2007). High Mn/Fe ratios have been observed in the centre of concretions from the Kimmeridge Clay formation with decreasing ratios as the concretion grows (Astin and Scotchman, 1988, Scotchman, 1991, Scotchman, 1989, Scotchman et al., 2000). This is observed in the type 2 concretion samples of F3 and F1 respectively. This suggests pore waters favoured Mn sequestration into the calcite cements rather than Fe. This suggests the precipitation of calcite occurred below the redoxcline with conditions
evolving towards a system that favours Fe precipitation within the cements (Coleman and Raiswell, 1995, Coleman, 1985, Curtis, 1977).

4.4.2.5 Implications on diagenesis in the Lower Eagle Ford Fmn

The results of this study highlights the number of factors that have affected the diagenesis of the Lower Eagle Ford Fmn. Numerous complex interactions control the formation of organic-rich mudstone, concretions and continuous limestone beds within the Lower Eagle Ford Fmn. Overall, this chapter has shown how diagenesis can be highly variable within a small stratigraphic section (10m of outcrop). The features discussed in this chapter (organic rich mudstones and Types 1, 2, 3 and 4 concretions) have all been influenced by diagenesis, but by varying degrees and by some processes more than others. The Type 2 concretions are the only features that are purely diagenetic.

The other concretions (Types 1, 3 and 4) and the organic-rich mudstones are primarily diagenetic. However, marine carbonate input, sediment input, sea level variation, primary productivity and tectonic/volcanic activity are all primary factors that have had an effect on the diagenetic processes that took place in the formation. All of the factors mentioned above bare an effect on carbonate precipitation in the Lower Eagle Ford Fmn and organic matter preservation, with a change of oxygen content in the water column not necessary for the precipitation of carbonate concretions within the organic-rich mudstones and/or the destruction of organic matter within the concretions.

This chapter also highlights, that despite the thesis focusing on small scale techniques such as petrographical and geochemical analysis, a full understanding of the depositional environment (basin dimensions, tectonic features), regional conditions (climate, primary productivity rates, tectonic activity), are imperative to fully understand the extent of burial diagenesis in highly heterogeneous formations like the Eagle Ford Fmn. Other outcrop studies of the Eagle Ford Fmn, such as (Minisini et al., 2014), suggest organic-rich mudstone/concretion cycles were driven by high frequency (fifth order scale) eustatic sea level fluctuations with spatial regularity between the various concretions consistent with orbital forced induced sea level change. While this is a thorough study addressing the impacts of Milankovitch cycles and sea-level variation on the Eagle Ford Fmn, there is no attempt to address 1) the impacts of diagenesis precipitating carbonate, preserving/destroying organicm matter 2) bentonite beds underlying the larger limestone beds, and 3) the overall effects volcanic activity may have had on the depositional environment e.g. primary productivity rates (Elder, 1988, Elder and Kirkland, 1994).
High frequency (fourth and fifth order scale) eustatic sea level fluctuations were likely to have had a key impact on carbonate precipitation on the sea floor. Carbonate beds correlate to possible fourth and fifth order scale cycles in chapter 2 of this thesis. However, what is ignored in other studies, such as Minisini et al., 2014, is; when bentonite beds are present directly below limestone beds as observed in outcrop, the carbonate beds are substantially thicker than the concretions/limestones beds which do not have bentonite beds below them. This indicates volcanic activity must have had an impact on carbonate precipitation and burial diagenesis in the southern Western Interior Seaway.

While petrographic studies are highly valuable because they can help identify specific processes that have created particular mineral compositions, textures and physical properties such as porosity and permeability. This chapter highlights the need to incorporate all levels of investigation from the micro-scale to basin scale to fully understand how organic-rich formations like the Eagle Ford Fmn are deposited and buried.

4.5 Conclusions

Source rocks containing mudstone/limestone cycles, such as the Kimmeridge Clay formation in the UK, only contain sub-metre spherical concretions (Astin and Scotchman, 1988). The Natih-B member in Oman, contains continuous limestone beds within organic rich mudstones but has no isolated sub-metre concretions. The Eagle Ford Fmn leaves an excellent opportunity to study the mechanisms that create sub-metre concretions and extensive limestone beds in fine grained sedimentary rocks. The abundance of marine derived carbonate in both the organic-rich weakly laminated mudstones and the four concretion types, highlight the overall low siliciclastic sediment supply throughout the Eagle Ford Fmn, creating a calcareous mudstone. Eustatic sea level changes, early diagenetic processes mainly involving sulphate reduction and volcanic activity play a key role in controlling lithofacies variability within the source rock-bearing succession. A variation in bottom water anoxia is often assigned to lithofacies variability, but in this case seems to have no evidential effect (Murris, 1981, Al Balushi, 2013, Scott, 1993, Scott, 1995, Scott, 1999, Droste and van Steenwinkel, 2004, Philip et al., 1995).

The presence of significant bentonite beds below the type 1 and type 4 concretions with sharp contacts, suggests carbonate precipitation immediately preceded a significant volcanic event. A
large increase of iron into an open marine environment caused an increase of planktonic skeletal material due to higher quantities of trophic level predators in the surface waters.

A volcanic event is interpreted to have occurred during transgression which formed the type 1 concretions. With additional skeletal material accumulating on the seabed and sediment starvation due to transgression and a possible high stand, a significant (30cm thick) carbonate bed was precipitated throughout the Eagle Ford Fmn basin. The type 4 concretions are interpreted to have formed in similar conditions but without a significant reduction in sediment supply, which resulted in the formation of a thinner carbonate bed with distinctive sedimentary structures.

The type 3 concretions are interpreted to be formed syn-deposition and present on the seafloor. They are interpreted to be driven by high frequency sea-level variation that reduced sediment supply to the basin. Sporadic deposition of sediment left certain areas of the seafloor exposed allowing for microbial redox reactions to oxidise organic matter and precipitate carbonate. Like the type 4 concretions bottom water currents re-distributed sediment creating the sedimentary structures observed in outcrop but allowing the formation of lenticular, discontinuous concretions across a stratigraphic horizon.

The origin of the type 2 concretions is interpreted to be sulphate-reducing bacteria producing exopolymeric substances (EPS) that have colonised local areas of the lithology influencing the morphology, mineralogy and the rapid precipitation of carbonate. Local communities of EPS creating lithifying microbial mats are interpreted to have precipitated the type 2 concretions within the surrounding organic-rich weakly laminated mudstones where the environment was ideal for high quality source rock deposition. The effects of a bentonite bed underlying the type 2 concretions (and organic-rich weakly laminated mudstones), remains unclear.
5. Porosity Distribution in the Eagle Ford Formation
5.1 Introduction

In recent years, there has been renewed interest in fine grained sedimentary rocks. In particular, fine grained organic-rich source rocks, commonly described as mudstones, or the now preferred term; mudrocks (Macquaker et al., 2014, Taylor and Macquaker, 2014, Driskell et al., 2012). Organic-rich source rocks are now reservoirs. Hydrocarbon exploration and production companies are now able to extract economical quantities of oil and gas directly from the source rock, due to technological advances in horizontal drilling and high pressure hydraulic fracturing (Chen et al., 2012, Rahm, 2011, Matsutsuya, 2011, Driskell et al., 2012, Walls and Sinclair, 2011). Despite extensive use of new technology for the exploration and production of unconventional organic-rich reservoirs, much uncertainty remains concerning storage (porosity), migration and production (maturity, generation and expelling) of hydrocarbons in source rocks (Chen et al., 2012, Fishman et al., 2013b, Pommer et al., 2014, Dawson and Almon, 2010, Donovan et al., 2012, Driskell et al., 2012, Dubiel et al., 2012, Hsu and Nelson, 2002a). Pore type and size is critical regarding hydrocarbon storage and migration in unconventional reservoirs (Pommer et al., 2014, Fishman et al., 2013b, Curtis et al., 2011, Bowman, 2010). Understanding the physics and chemistry of light hydrocarbons within micro and macro-pores whether, in kerogen or in inorganic minerals, is key to improving stimulation techniques and overall production in unconventional reservoirs (Chen et al., 2012, Walls and Sinclair, 2011, Fishman et al., 2013b).

The aim of this chapter is to explore pore type and pore size distribution throughout the Eagle Ford Fmn. Samples from six lithofacies (1-3 and 5-7) from the lithofacies scheme (Table 5.1), described in Chapter 2, will be used to identify porosity type and size distribution in the Eagle Ford Fmn. The lithofacies represent >90% of total rock volume in the Eagle Ford Fmn and differentiate between mineralogical variation, which is thought to impact porosity distribution (Rine et al., 2013, Fishman et al., 2013b). The lithofacies studied are:

9. Argillaceous Mudstones
10. Weakly laminated Mudstones
11. Laminated Foraminifera rich Wackstones
5  Skeletal Wackstone to Packstones
6  Bioturbated Lime Mudstone to Wackestones
7  Recrystallised Foraminiferal dominated Packstone to Grainstones

**5.2 Methods**

Detailed petrographic observations of 12 carbon-coated (two per lithofacies), 20µm cut thin sections sampled from the Late Cretaceous Eagle Ford Fm (Table 5.0). Samples were selected by thin section quality and ability to apply an even carbon-coating across the thin section. Therefore, samples come from a wide range wells and outcrop samples (Table 5.0 and Figure 5.0).

Each was studied using a Philips XL30 ESEM-FEG fitted with an EDAX Genesis EDS system. Backscattered and second electron images were obtained under high vacuum mode with an accelerating voltage of 15kV. All samples were cut and prepared at Statoil ASA, Bergen, Norway. Rock-Eval analysis was undertaken on 22 samples from the Eagle Ford Fmn to obtain TOC (%Wt) and thermal maturity (see table 5.0). Six core plugs were available for He-porosimetry measurements to obtain total porosities from some of the lithofacies (table 5.0). Rock-Eval analysis and He-porosimetry were performed at Statoil ASA, Bergen, Norway. All samples have a thermal maturity of ~0.9 Ro%.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lithofacies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell J A Leppard 1-H, 13685.30 ft</td>
<td>Argillaceous Mudstones</td>
</tr>
<tr>
<td>D1S1-ML-M-MB1, outcrop sample</td>
<td>Argillaceous Mudstones</td>
</tr>
<tr>
<td>Shell J A Leppard 1-H, 13598.0 ft</td>
<td>Weakly laminated Mudstone</td>
</tr>
<tr>
<td>D2S3-LL-M, outcrop centre</td>
<td>Weakly laminated Mudstone</td>
</tr>
<tr>
<td>DMS1 20m E block 2A, outcrop sample</td>
<td>Laminated Foraminiferal-rich Wackstone</td>
</tr>
<tr>
<td>D1S1-ML-M-MB1, outcrop sample</td>
<td>Laminated Foraminiferal-rich Wackstone</td>
</tr>
<tr>
<td>J W Blumberg 7243.6 ft</td>
<td>Skeletal Wackestones to Packstones</td>
</tr>
<tr>
<td>J W Blumberg 7241.4 ft</td>
<td>Skeletal Wackestones to Packstones</td>
</tr>
<tr>
<td>Matthews J-L 1-1 101</td>
<td>Bioturbated lime mudstone</td>
</tr>
<tr>
<td>Matthews 4673.80 ft</td>
<td>Bioturbated lime mudstone</td>
</tr>
<tr>
<td>J W Blumberg 7285ft</td>
<td>Recrystallised Foram dominated Packstone to Grainstones</td>
</tr>
<tr>
<td>H-P Orts 2 7678.50 ft</td>
<td>Recrystallised Foram dominated Packstone to Grainstones</td>
</tr>
</tbody>
</table>
Table 5.0. Table of samples used in study. 12 carbon-coated (two per lithofacies), 20µm cut thin sections sampled from the Late Cretaceous Eagle Ford Fmn

Each thin section was imaged at x1000 magnification. Any porosity visible at this magnification was recorded, although very rare. The image at x1000 magnification created a working area of equal size which could easily be applied to each sample analysed under the Scanning Electron Microscope (SEM). Higher magnifications at x5000, x12000 and x25000 could then be used to identify and record macro and micro-porosity within the working area (Figure 5.1). This process was then repeated in a different area of each sample. 1758 pores and their types and size were recorded, starting in the top left corner of the working area towards the bottom right corner. Pores were classified using the IUPAC nomenclature (micro < 2µm, macro 2 -50µm and meso > 50µm pores). Pores were also separated by a simple scale of 50-100nm, 100-500nm, 500-1µm, 1µm-1.1-5µm, 1.5-2µm, 2-5µm and >5µm respectively.
<table>
<thead>
<tr>
<th>Well Name</th>
<th>GPS Location</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Latitude</td>
<td>Longitude</td>
<td></td>
</tr>
<tr>
<td>Matthews J L 1-1</td>
<td>29.2053</td>
<td>-100.9026</td>
<td></td>
</tr>
<tr>
<td>Wagner Bros Inc 11</td>
<td>29.2264</td>
<td>-100.0139</td>
<td></td>
</tr>
<tr>
<td>Lloyd Hurt 1</td>
<td>29.2197</td>
<td>-99.7624</td>
<td></td>
</tr>
<tr>
<td>Statoil/Talisman-1</td>
<td>29.1984</td>
<td>-99.9651</td>
<td></td>
</tr>
<tr>
<td>Shell J A Leppard 1-H</td>
<td>29.2263</td>
<td>-98.9145</td>
<td></td>
</tr>
<tr>
<td>J W Blumberg</td>
<td>29.3797</td>
<td>-98.8623</td>
<td></td>
</tr>
<tr>
<td>W Bretchell</td>
<td>29.3615</td>
<td>-98.0226</td>
<td></td>
</tr>
<tr>
<td>Shell Hay E-D 1</td>
<td>29.2381</td>
<td>-97.4962</td>
<td></td>
</tr>
<tr>
<td>H-P Orts 2</td>
<td>29.4530</td>
<td>-97.4919</td>
<td></td>
</tr>
<tr>
<td>Road cut location on Highway 90</td>
<td>29.3797</td>
<td>-101.2038</td>
<td></td>
</tr>
</tbody>
</table>

*Figure 5.0. A. Location map and table of GPS coordinates. Map denotes all Eagle Ford Fmn well locations across southern Texas (green circles) used in this study. The hollow yellow polygons denote the locations where the Eagle Ford Fmn outcrops in southern Texas. Red polygon denotes the general area of outcrops which were studied. Hollow blue polygons denote the Austin Chalk locations across southern Texas.*
Although all areas in each sample was examined, undoubtedly some sample bias exists towards areas of higher pore density. This is true for the clay and organic-rich lithofacies where clay held porosity and organic porosity have a high density where clay minerals or organic matter have precipitated. Backscattered (BSE) images were used to show compositional variations while secondary electron (SE) images highlight topography, such as cements overgrowths and depressions caused by pores.

Figure 5.1. Schematic of the working area used for detailed petrographic analysis of each sample. The working area is denoted by an x1000 magnification image. Higher magnifications can then be used within the area to identify meso and macro porosity.

Pores were measured using a simple technique using the scale bar displayed on the SEM screen and a ruler. Very thin, but elongated pores had their biggest axis measured. This was decided due to its simplicity, speed, and limitations of using samples which were not Ar-ion milled and using a standard ESEM. Measuring pores down to 10s of nanometres without Ar-ion milled samples or a FIB-SEM is notoriously difficult due to the inability to create sufficient resolutions to identify pores (Pommer et al., 2014, Walls and Sinclair, 2011, Bust et al., 2013).
<table>
<thead>
<tr>
<th>Lithofacies</th>
<th>Main minerology (XRD) % (average)</th>
<th>Colour</th>
<th>Main Grains Present</th>
<th>Sedimentological Characteristics</th>
<th>TOC (wt%)</th>
<th>Avg %</th>
<th>Φ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argillaceous Mudstone</td>
<td>29 (22 - 36)</td>
<td>Black to very dark green/brown</td>
<td>Mixed layer I/S. Kaolinite/chlorite, planktonic (globigerinid) foraminifera</td>
<td>Faintly laminated- sometimes massive. Ripple laminae are common. Some burrowing is present but extremely rare.</td>
<td>0.3</td>
<td>3.35</td>
<td>6.4</td>
</tr>
<tr>
<td>Weakly laminated Mudstone</td>
<td>47 (31-55)</td>
<td>Black</td>
<td>Mixed layer I/S. Kaolinite/ chlorite, planktonic (globigerinid) foraminifera. Inoceramid bivalves</td>
<td>Thin (sub mm) planar but truncated laminae. Some are wavy but are only present at the bottom of packages where they transition from the Argillaceous Mudstones Contain sharp or erosive contacts.</td>
<td>-5</td>
<td>4.21</td>
<td>7.84</td>
</tr>
<tr>
<td>Laminated Foraminifera-rich Wackestones</td>
<td>62 (52-76)</td>
<td>Medium to dark Grey</td>
<td>Mixed layer I/S. Globigerinid planktonic foraminifera and benthic foraminifera. Calcite cements. Kaolinite</td>
<td>Planar laminated. Laminations consist of foraminifers. Some laminae resemble ripples, although this is rare. Burrowing is present.</td>
<td>-4</td>
<td>3.25</td>
<td>5.01</td>
</tr>
<tr>
<td>Recrystallised Lime Wackestones (crystalline)</td>
<td>90 (79-94)</td>
<td>Light Grey</td>
<td>Recrystallised carbonate cements cements</td>
<td>Highly cemented with calcium carbonate. Crystalline texture. Cement grains in size from 20-100µm. Fractures are infilled and closed with carbonate, though rare.</td>
<td>-</td>
<td>0.06</td>
<td>0.08</td>
</tr>
<tr>
<td>Skeletal Wackestone to Packstones</td>
<td>73 (65-86)</td>
<td>Medium to light grey</td>
<td>Fragmented Inocerarmid bivalves, Globigerinid foraminifera, Pelooids, phosphate grains. Fish bones and teeth.</td>
<td>Strongly laminated and bedded. Cross laminations and imbricated bedding. Scour and truncated laminae surfaces. Skeletal fragments most dense at base of units and become more rare- fining up.</td>
<td>0.3</td>
<td>0.29</td>
<td>7.29</td>
</tr>
<tr>
<td>Bioturbated Lime mudstone to Wackestone</td>
<td>84 (76-88)</td>
<td>Dark grey to light grey</td>
<td>Bivalves, foraminifera, radiolarians and unidentified skeletal material.</td>
<td>Bioturbated. Moderately recrystallised with calcium carbonate. Fractures are infilled and closed with carbonate, though rare. Skeletal fragments are calcified, some are phosphatosed, though rare.</td>
<td>0.3</td>
<td>0.64</td>
<td>2.45</td>
</tr>
<tr>
<td>Foraminifer dominated Packstone to Grainstone</td>
<td>89 (85-98)</td>
<td>Light grey</td>
<td>Carbonate cements. Benthic foraminifera, unidentified skeletal material</td>
<td>Recrystallised. Fractures are infilled with calcium carbonate. Commonly interbedded with skeletal wackestones and packstones.</td>
<td>0.3</td>
<td>0.18</td>
<td>0.30</td>
</tr>
<tr>
<td>Bentonite (Volcanic Ash)</td>
<td>10 (n=1)</td>
<td>Green-grey-yellow</td>
<td>Bioclasts, large skeletal fragments and teeth.</td>
<td>Commonly massive, although some beds do contain planar laminae. Heavily bioturbated.</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 5.1. Summary of the Eagle Ford Fmn lithologies, showing mineralogical composition, colour, sedimentological characteristics, total organic carbon (TOC), and porosity (Φ). In this chapter, we will only focus on lithofacies 1, 2, 3, 5, 6 and 7.
5.3 Results

A total of 1758 pore measurements were conducted in this study. There are three types of porosity which have been identified in the six lithofacies present within the Eagle Ford Fmn. (1) Organic matter-hosted porosity (Figure 5.2). (2) Clay mineral hosted porosity (figure 5.2). (3) Intra and inter-crystalline porosity present between and within carbonate cements, quartz cements and biogenic debris (figure 5.3).
Figure 5.2. Bar charts displaying porosity type and pore size distribution across the three lithofacies of the Eagle Ford Fmn. The organic and clay rich lithofacies contain significantly more meso porosity. The smallest pores (50-100nm) are mainly observed in clay minerals, with some present within organic material. Organic matter-hosted porosity observed in organic rich lithofacies (1-3) is larger, with typical pore sizes 100-500nm. Lithofacies containing more authigenic carbonate cements have a different pore type and pore size distribution. Intra-crystalline porosity is main pore type. These pores are typically larger, though not as frequent compared to clay-held porosity. Hence, lower pores counts overall in the carbonate rich lithofacies.

### 5.3.1 Argillaceous Mudstones

The argillaceous mudstones are clay rich, contain TOC values of 5-7% and contain the least carbonate (Table 5.1). The main porosity type in this lithofacies is clay-hosted porosity, 65%, and organic matter hosted porosity, 29%, (Figure 5.2). Intra-crystalline porosity is rare (5%) and is only present within authigenic carbonate cements which infill foraminifera tests and micro-quartz cements present in the matrix (Figure 5.2). Inter-crystalline porosity is extremely rare, with only two pores identified contributing a negligible amount (0.5%) to the porosity count. 48% of pore sizes are between 100-500nm in the argillaceous mudstones. Nearly all organic-porosity is 100-500nm in diameter (Figure 5.1. The rest of the 100-500nm pores are large clay mineral pores. 35% of the total pore count is 50-100nm in size. All of these pores are exclusively clay-held porosity. 10% of the pore sizes are 500nm-1µm, with the remaining 4% and 3% 1-1.5µm and 1.5-2µm respectively (Figure 5.1). These larger pores are seen in organic matter and within carbonate minerals as intra-particle porosity.

### 5.3.2 Weakly Laminated Mudstones

The weakly laminated mudstones are relatively clay rich ( average 27%) and the most organic rich (TOC 5-8%) of the lithofacies present in the Eagle Ford Fmn. 40-60% of the composition is carbonate held within the matrix as coccolith fragments and authigenic infilling cements (Table 5.1). The main porosity type in this lithofacies is also clay-hosted porosity (48%) and organic porosity (37%). There is more organic matter hosted porosity in this lithofacies compared to the argillaceous mudstones due to more organic matter observed in the weakly laminated mudstones.
(Figure 5.2). Intra-crystalline porosity is more common (14%) due to more carbonate.

Figure 5.3. SEM-BSE micrographs of organic matter-hosted porosity within the Argillaceous Mudstones (1), Weakly Laminated Mudstones (2) and Laminated, Foraminiferal rich Wackestones (3). A. Shell J A Leppard 1-H, 13685.30 ft of an argillaceous mudstone. At the left of the image, stringy organic matter between authigenic quartz and mixed layer I/S with 500nm-1µm pores (red circle). At the bottom of the same image a 100-500nm pore is visible. B. Shell J A Leppard 1-H, 13598.0 ft of an weakly laminated mudstone. SEM-SE image of organic matter surrounded by
authigenic calcite cements with typical 100-500nm pores (red circle), at the boundary of organic matter and mineral surfaces. C. Shell J A Leppard 1-H, 13598.0 ft. Stringy organic matter surrounded by silicate and carbonate grains displaying 50-100nm pores (red circle) and 100-500nm pore. D. DMS1 20m E block 2A, outcrop sample of a laminated foraminiferal-rich wackestone. Large (1.1-1.5µm), elongated pores on mineral boundaries. E. D1S1-ML-M-MB1, argillaceous mudstone. Organic matter containing pores of varying size. Most are 100-500nm with the rest 50-100nm. F. D2S3-LL-M weakly laminated mudstone. Foraminifera infilled with organic matter. A large shelter-like pore present by the mineral surface boundary (red circle).

infilling foraminifera tests present in the assemblage. Like the argillaceous mudstones, there is negligible inter-crystalline porosity, <0.5% (Figure 5.2). Pores 100nm-500nm in size contribute to 40% of the pore size distribution. All observed pores this size are present within clay minerals and organic matter (Figure 5.2 and 5.3). Pores between 50-100nm constitute 24% of the pore size distribution and are mainly found in clay minerals, with some pores observed in organic matter. Pores 500nm-1µm constitute 18% of the pore size distribution and are almost exclusively observed within organic matter in the weakly laminated mudstones. These pores are all observed within organic material at mineral surface boundaries, usually the walls of foraminifer tests or authigenic quartz cements (Figure 5.3). The weakly laminated mudstones contain higher quantities of larger pores, 11% and 5% for 1-1.5µm and 1.5-2µm respectively, compared to the argillaceous mudstones.

5.3.3 Foraminiferal-rich Wackestones

The laminated foraminiferal-rich wackestones contain less clay (average 14%) and organic matter (average 4% TOC), compared to the weakly laminated mudstones, but contain considerably more carbonate (average 62%) due to authigenic carbonate infilling foraminifers (Table 5.1). In this lithofacies there is a small decrease of clay-hosted porosity (41%) compared to the previous clay rich lithofacies (Figure 5.3). However, the biggest decrease is seen in the quantity of organic matter porosity at 15%, (Figure 5.3). Intra-crystalline porosity is much more common, with 38% of the pore count now seen within carbonate cements. Due to an increase in carbonate content, inter-crystalline porosity is observed, but rare (3%). Nearly all inter-crystalline porosity has been filled with authigenic clay minerals and bitumen (Figure 5.2 and 5.3). Pore size distribution is similar to the weakly laminated mudstones, however, all the 50nm-100nm pores observed were clay-hosted pores,
while the 100-500nm pores were either clay-hosted or organic matter hosted (Figure 5.2 and 5.3). All organic matter-hosted pores were observed at mineral surface boundaries within foraminifera tests (Figure 5.2). The majority of larger pores, (500nm-1µm and above) are observed at intra-crystalline porosity within carbonate cements (Figure 5.5).

### 5.3.4 Skeletal Wackestone to Packstones

The skeletal wackestones to packstones contain less carbonate and more clay than the laminated foraminiferal rich wackestones. However they contain less TOC (Table 5.1). Due to a decrease of organic carbon content, organic matter-hosted porosity has significantly decreased (4%), compared to the previous three lithofacies (Table 5.1).

Clay-hosted meso and macro porosity constitutes 39% of the pores, which are all present within the micritic matrix, which surrounds the biogenic grains and skeletal debris. Inter-crystalline porosity is present but very rare (<1%). The bulk pore type is intra-crystalline porosity, seen within carbonate cements and skeletal fragments. Some pores are over 50µm in diameter while most pores within skeletal fragments are over 10µm in diameter (Figure 5.2). The main quantity of pores however, is present within carbonate cements (Figure 5.4 and 5.5). Pore size distribution changes dramatically in the skeletal wackestones to packstones, with significant increase in the quantity of micro porosity and a decrease in meso porosity (Figure 5.5). The skeletal wackestones to packstones contain the largest pores observed in the Eagle Ford Fmn. All pores over >5µm are observed within skeletal fragments. Total porosity figures for this lithoacies are unknown (Table 5.1).
Figure 5.4. SEM-BSE micrographs of clay-hosted porosity (CHP) within the Argillaceous Mudstones (1), Weakly Laminated Mudstones (2) and Laminated, Foraminiferal rich Wackestones (3). A. Shell J A Leppard 1-H, 13598.0 ft. Matthews J L 1-1 4673.50 of an argillaceous mudstone. Clay hosted intra porosity between illite grains. Pores are elongated but are classed as 50-100nm macropores. B. Matthews J-L 1-1 4673.50 ft. Clay hosted porosity within a foraminifera test. Chlorite grains have morphed from kaolinite and contain meso-porosity (red circles). C. Matthews J-L 1-1 4673.50 ft. 100-500nm macropores present between mineral boundary surfaces (quartz and kaolinite). D. D1S1-ML-M-MB1, argillaceous mudstone. Chlorite grains within the matrix or an argillaceous mudstone with 50-100nm pores within the wispy grains. Larger 100-500nm pores are present (red arrows), between the main grains. E. D2S3-LL-M weakly laminated mudstone Kaolinite grain within the
matrix with mineral boundary surface porosity at the top and bottom of the grain. The pore at the top is between recrystallised coccolith fragments and kaolinite. While the bottom is between kaolinite and a mixture of coccolith fragments, carbonate micro cements and illite. F. D1S1-ML-M-MB2. Kaolinite infills porosity within coccolith debris. Pores are present between the kaolinite books and at the boundary of coccolith surfaces.

Figure 5.5. SEM-BSE micrographs of inter (IEP) and intra-particle porosity (IAP) within the Skeletal Wackestones to Packestones, Bioturbated Lime Mudstone to Wackestone and Recrystallised Foram dominated Packestone to Grainstones. A. Matthews J-L 1-1 101 bioturbated lime mudstone. Intra-particle pore (IAP) within calcite cements, which have infilled and surrounded foraminifera
tests. B. Matthews J-L 1-1 101 bioturbated lime mudstone. Intra-particle macro pore (IAP) within authigenic calcite and quartz cements and illite grains. Note these pores are generally much larger (1-3µm). C. Matthews J-L 1-1 4673.50 ft. Authigenic calcite cements infill a foraminifera test. A 3-4µm wide intra-particle pore (IAP) is present between the cement grains. D. J W Blumberg 7285 ft. Recrystallised Foram dominated Packstone to Grainstones. Extensive isopachous authigenic calcite and quartz cements overprint a bioturbated lime mudstone to wackestone. ~3% of the porosity in this lithofacies is inter-particle porosity (IEP). Pores are rarely seen between cement grains. Nearly 2/3 of the porosity is intra particle porosity (IAP). E. J W Blumberg 7243.6 ft. Skeletal Wackestones to Packstones. A large (>50µm) intra-particle macropore within a skeletal fragment in a skeletal wackestone to packstone. F. J W Blumberg 7243.6 ft, Skeletal Wackestones to Packstones. Multiple intra-particle (IAP) macropores over 5µm in diameter within a skeletal fragment. These pores are thought to contribute a significant amount of porosity to the skeletal wackestones to packstones.

5.3.5 Bioturbated Lime Mudstones to Wackestones

The bioturbated lime mudstones to wackestones contain no organic matter-hosted porosity (figure 5). 69% of porosity is observed at intra-crystalline porosity within calcite and quartz cements. Clay minerals make only 18% of the bioturbated lime mudstone to wackestone composition, but are observed to obtain 35% of the pore type distribution. Inter-crystalline porosity is observed between cement and biogenic grains, but is stressed these types of pores are rare. Overall pore counts decrease (143) for this lithofacies. He porosimetry indicates total porosity for this lithofacies is 2-4%. Due to a lack of organic porosity and clay minerals, 50-100nm and 100-500nm pores are rare (6% and 9% respectively). Pore sizes 500-1µm, 1-1.5µm and 1.5-2µm are more frequent (20%, 23% and 33% respectively), which are all present as intra-crystalline pores within authigenic cements (Figure 5.5).

5.3.6 Recrystallised foraminifera packstone to grainstones

The recrystallised foraminifer’s packstone to grainstones contain no organic or clay-held porosity (Figure 5.2). This lithofacies is dominated by authigenic calcite cements infilling foraminifers (table 1). Intra-crystalline porosity contributes to 98% of the pore type distribution, with inter-crystalline porosity making the remaining 2%. Like the bioturbated lime mudstones to wackestones, overall porosity counts are
lower compared to previous lithofacies, 113 (Figure 5.5). The largest mesopores observed were 500nm-1µm pores and were the only mesopores to be observed in this lithofacies (Figure 5.2). Small micro-pores (1-1.5µm) are present, but only comprise 11% of the pore size distribution (figure 5). 42% of the pore size distribution is relatively large 2-5µm pores (figure 5).

5.4 Interpretation and Discussion

The Eagle Ford Fmn is a carbonate rich mudstone, which contains varying quantities of carbonate throughout the formation (see chapter 1) (Driskell et al., 2012, Robison, 1997, Liro et al., 1994, Donovan et al., 2012, Hsu and Nelson, 2002a, Martin et al., 2011). Porosity types are influenced by varying amounts of carbonate, clay minerals, and organic matter present in each lithofacies and their maturity (Fishman et al., 2013b, Fishman et al., 2013a, Pommer et al., 2014, Rine et al., 2013).

Lithofacies with high clay and organic content result in a pore type distribution dominated by clay and organic-hosted meso-porosity with pore sizes ranging from 100-500nm. Organic-porosity was mainly observed as 100-500nm pores at mineral surface boundaries inside foraminifers, diatoms and expelled bitumen (post mineral diagenesis) within the matrix. Rine et al., 2013 and Pommer et al., 2014 report similar findings in low maturity (0.7-0.9 Ro%) samples, where organic matter pores had a circular diameter of ~100nm, but also often located at mineral surface boundaries. Clay-held pores have a wide range of pore diameter of 50-500nm. But, are generally smaller compared to organic matter porosity, with pores between 60-120nm. Pommer et al., 2014 state similar ranges in clay-held porosity size, but conclude smaller clay mineral pores under 100nm were only observed in higher maturity samples (1.2-1.3Ro%). Variations in clay mineral porosity are caused by variations in detrital clay input and clay diagenesis (Schieber et al., 2010, Aagaard and Jahren, 2010, Yang and Aplin, 2009, Dawson and Almon, 2010, Walls and Sinclair, 2011).

Other porosity type distribution studies (Pommer et al., 2014, Rine et al., 2013, Fishman et al., 2013b, Fishman et al., 2013a) state organic porosity is the most common pore type observed in the Late Cretaceous Eagle Ford Fmn. Rine et al 2013
demonstrate how porosity in some shale gas formations, such as the Barnett Shale in the northeast of the USA, is entirely organic-porosity. However, this study shows clay mineral porosity is the most common type in the Eagle Ford Fmn. Low maturity samples (0.9 Ro%), have not fully undergone hydrocarbon generation and expulsion, which allows the development of secondary porosity in the organic matter (and bitumen) (Bust et al., 2013, Pommer et al., 2014). Therefore there were fewer organic-pores compared to clay mineral held pores. In higher maturity samples, which were used in past studies, secondary pores within organic matter are a lot more common due to additional generation and expulsion of hydrocarbons (Pepper and Corvit, 1995, Pommer et al., 2014). Secondary pores have a range of pore shapes and sizes, from equant 4nm to 450nm complex irregular shapes (Pommer et al., 2014, Rine et al., 2013). These types of organic-pores were not observed in our study. This could be due to the maturity of the samples, but also the methods used to carry out the study, which were not capable of capturing the smaller pores within the organic matter. Imaging and measuring pores up to nanometres requires Ar-ion milled samples and a focus ion beamed (FIB) SEM. (Pommer et al., 2014, Fishman et al., 2013b, Fishman et al., 2013a, Rine et al., 2013). These techniques produce much better quality images which allow for higher magnifications and contrasts (grey scale) between organic matter and pore edges. However a disadvantage of this technique is sample size. Samples sizes for FIB-SEM are an order of magnitude smaller than the already small standard thin section for standard SEM use. An advantage of using an entire thin section at is; it’s more likely to represent the lithofacies and porosity type distribution in general.

The carbonate-rich lithofacies (5-7) contain a different pore type distribution compared to the clay-rich and organic-rich lithofacies (1-3). The laminated foraminiferal rich wackestones are regarded as a source rock lithofacies due to their organic carbon content (table 1). However, their pore distribution is different compared to lithofacies 1 and 2 due to authigenic cements infilling foraminifers (Figure 5.2). The carbonate rich lithofacies (5-7) contain significantly larger pores compared to the clay rich lithofacies (figure 5). Porosity counts (frequency) are less in all carbonate rich lithofacies compared to the organic and clay rich lithofacies, especially in lithofacies 6 and 7. This observation correlates with He porosimetry measurements that indicate total porosity is less in lithofacies 6 (4%) and 7 (2-3%).
(Table 1). Using the assumption that decreasing clay and organic porosity with increasing intra-crystalline porosity, overall decreases total porosity; it is sensible to assume the laminated foraminiferal wackestones (lithofacies 3), and skeletal wackestones to packstones (lithofacies 5), have a total porosity that lies between lithofacies 1-2, and lithofacies 6-7.

The middle section Eagle Ford Fmn which comprises of the upper Lower Eagle Ford Fmn and lower Upper Eagle Ford Fmn, is mainly composed of Skeletal Wackestones to Packestones and Bioturbated Lime Mudstones to Wackestones with interbedded Laminated rich Wackestones and Weakly laminated Mudstones (Figure 5.6). Due to lithofacies distribution, the porosity distribution of the Middle Eagle Ford Fmn is found within intra-crystalline and clay-hosted porosity. The Upper Eagle Ford Fmn is composed of Bioturbated Lime Mudstones to Wackestones, Foraminiferal dominated Packstones to Grainstones with interbedded Skeletal Wackestones to Packstones (Figure 5.6). Here the pore network is entirely intra-crystalline porosity. Over 80% of Lower Eagle Ford Fmn, is composed of Argillaceous Mudstones, Weakly Laminated Mudstones, Laminated Foraminiferal rich Wackestones. These lithofacies are interbedded with thin Bioturbated Lime Mudstones to Wackestones. Here the bulk of porosity is observed as meso-scale clay-held and organic-held porosity types in this section of the formation (Figure 5.5).

Larger intra and inter-crystalline macro pores within the carbonate-rich lithofacies are significant because macropores this size are likely to represent interconnected porosity, resulting in permeability (Fishman et al., 2013b, Bust et al., 2013). Fishman et al., 2013 carried out laboratory experiments where porosity within samples similar to the bioturbated lime mudstone to wackestones (lithofacies 6), had total porosities of 6%, and permeability ranges from 300-1000nD (Fishman et al., 2013b, Fishman et al., 2013a). The organic-rich mudstones (similar to lithofacies 1-2), contained higher total porosities of 7-10%, but significantly less permeability, 20-100nD (Fishman et al., 2013b). Larger intra-crystalline porosity also had an impact on hydrocarbon storage and the impacts it had on the availability of “free” hydrocarbons for extraction. The organic-rich mudstone's contained the best storage due to higher total porosities within organic matter (intra-bitumen). A significant quantity of free hydrocarbons (mainly gas) can be present within kerogen. However this is conditional on the size and quantity of the kerogen pores (intra-kerogen),
Figure 5.6. Idealised well logs of the Eagle Ford Fmn with mineralogical (carbonate and clay) and TOC variation. The Lower Eagle Ford Fmn and lower Middle Eagle Ford Fmn is composed of

Optimum target area

TOC 2-3%

Intra and Inter-crystalline interconnected macro-pores

<table>
<thead>
<tr>
<th>Austin Chalk</th>
<th>Lower EF</th>
<th>Middle EF</th>
<th>Upper EF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithofacies</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clay %</td>
<td>0</td>
<td>45</td>
<td>26</td>
</tr>
<tr>
<td>CaCO %</td>
<td>98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOC %</td>
<td>7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Argillaceous Mudstone
- Weakly laminated Foraminiferal Mudstones
- Laminated Foraminifera rich Wackestones
- Skeletal Wackestone to Packstones
- Bioturbated Lime Wackestones
- Foraminifera dominated Packstone to Grainstone
- Bioturbated Bentonite (volcanic ash)
organic, clay-rich lithofacies (lithofacies 1, 2 and 3), with thin interbedded bioturbated lime-
mudstone to wackestones (lithofacies 6). Porosity in the lower Eagle Ford is observed as meso-scale
clay-hosted and organic porosity. The Middle Eagle Ford Fmn consists of a mixture of lithofacies 2,
3, 5 with thin interbeds of lithofacies 6, giving a pore network observed mainly in clay-held porosity
and intra-crystalline porosity. The Upper Eagle Ford Fmn consists of lithofacies 6 and 7 interbedded
with lithofacies 3 and 5. Here porosity networks are entirely seen as intra-crystalline porosity with
carbonate cements and biogenic material.

which is a function of thermal maturity (Bust et al., 2013). In low maturity samples,
free gas will occur mostly in the inorganic intra-crystalline pores, which was
expelled during early maturation and generation (Bust et al., 2013). Only in
thermally mature samples (>1.5Ro%), where extensive hydrocarbons have been
expelled from the kerogen, does sufficient porosity form where free gas can migrate
and/or be stored and therefore be released via hydraulic stimulation (Bust et al.,
2013).

In thermally immature organic-rich samples however, Fishman et al., 2013b showed
stored hydrocarbons are geochemically associated with the S2 peak in RockEval
pyrograms, where hydrocarbons are locked in the bitumen. Essentially these
hydrocarbons are not accessible via hydraulic fracturing and can only be released
through maturation. Therefore immature organic-rich lithologies are unlikely to yield
significant quantities of hydrocarbons via hydraulic stimulation. Fishman et al.,
2013b also showed, the carbonate-rich lithologies contain a much smaller S2 peak,
but display a much larger S1 peak, indicating a much greater amount of “free”
hydrocarbons present relative to the organic-rich lithologies. Larger interconnected
pores with significant permeability allow migration and better storage of
hydrocarbons (Fishman et al., 2013b, Fishman et al., 2013a).

Although I have not specifically investigated the mechanical or full physical
properties of lithologies 1-7; I infer that exploration and production companies that
have acquired acreage in high thermally mature (>1.5-3 Ro%) areas of the Eagle
Ford Fmn, aim to stimulate the TOC rich, clay rich area of the formation. Here
porosity within the organic matter will be developed enough to produce economical
quantities of free hydrocarbons. Production companies which find themselves in
acreage with a thermal maturity between 0.5-1.5Ro% should aim for areas of the
Eagle Ford Fmn that contain higher quantities of carbonate, especially lithologies
similar to lithofacies 5 and 6. These lithofacies are likely to contain more free hydrocarbons available for extraction due to the larger storage capacity caused by intra-crystalline porosity within carbonate cements.

5.5 Conclusions

This high resolution petrographic study shows relatively immature (0.9 Ro%) Eagle Ford Fmn samples display small quantities of organic porosity developed through the maturation, generation and expulsion of hydrocarbons. The sampled organic-rich and clay rich lithofacies therefore have a porosity distribution dominated by mesoscale clay-hosted porosity and some organic held porosity. The carbonate-rich lithofacies which contain less organic matter, have a different porosity distribution. Intra-crystalline porosity within carbonate cements dominate the porosity distribution with pores an order of magnitude (>1µm) larger compared to the organic rich, clay rich lithofacies.

Mineralogy, organic content and thermal maturity are the main uncertainties for geoscientists to locate where “sweet spots” lie in the Eagle Ford Fmn and other shale gas reservoirs for hydraulic stimulation. Areas of stratigraphy (Middle Eagle Ford Fmn) consisting of carbonate-rich lithologies (lithofacies 3, 5, 6 and 7) may be the better units to target for hydraulic stimulation if exploration and production companies own acreage in relatively thermally immature depths. Clay-hosted mesoscale porosity is unlikely to produce any permeability or create significant porosity connectivity. Only larger, secondary porosity developed through thermal maturity within the organic matter (intrabitumen) is likely to produce significant storage for free hydrocarbons and permeability for hydrocarbons to flow. Therefore, areas of stratigraphy (Lower Eagle Ford Fmn) consisting of clay and organic-rich lithologies (lithofacies 1, 2 and 3) may be the better units to target for hydraulic stimulation if exploration and production companies are at thermally mature depths.
6. Summary
6.1 Introduction

The aim of this study was to build a better understanding of diagenesis in the Eagle Ford Fmn and how diagenesis affects reservoir properties. Key objectives were:

7. To identify and describe the lithofacies present in the Eagle Ford Fmn.
8. Discuss and describe the depositional environments which created the Eagle Ford Fmn.
9. To identify the diagenetic processes that occurred in the Eagle Ford Fmn and build a better overall understanding of mudstone diagenesis.
10. Investigate why concretions and laterally continuous limestone beds are present in the Lower Eagle Ford Fmn.
11. Discuss porosity types and their distribution between the lithofacies.
12. Discuss how all the above effects reservoir properties and where the best areas of the Eagle Ford (“sweetspots”) are to target for stimulation and production.

The main chapters (chapters 2, 3 4 and 5), within this study have addressed the key objectives mentioned above, regarding diagenesis, depositional environments, reservoir properties and the impacts these have on production within the Eagle Ford Fmn.

6.2 Chapter Summaries

6.2.1 Chapter 2: Lithofacies of the Eagle Ford Fmn

The first main chapter of this study (chapter 2) has addressed the varying mineral content observed throughout the Eagle Ford Fmn. Analysis of five Eagle Ford Fmn cores undertaken at the Bureau of Economic Geology (BEG), Austin, Texas, USA, along with analysis of 78 polished 20µm thin sections using standard microscopic techniques (including scanning electron microscopy - SEM) identified an idealised eight lithofacies:

12. Argillaceous Mudstone
13. Weakly laminated Mudstone
14. Laminated Foraminifera rich Wackstone
15. Recrystallised Lime Wackestones (concretions)
16. Skeletal Wackstone to Packstone
17. Bioturbated Lime Mudstone to Wackestone
18. Foraminiferal dominated Packstone to Grainstone

These lithofacies are part of a sequence stratigraphic model that is characteristic of periplatform carbonates that record sea-level fluctuation through carbonate production (Goldhammer et al., 1990, Goldhammer and Johnson, 2001, Grammer et al., 1993). The Eagle Ford Fmn-Austin Chalk records a 2nd order sequence. Within the 2nd order sequence there are two interpreted 3rd order sequences from the five cores analysed. The first 3rd order sequence represents the organic-rich, clay-rich lithofacies which are distributed in the lower section, with the second sequence in the upper section, which represents a decrease in TOC with increased carbonate content. Fourth and fifth order sequences are present in all cores but lack consistency between the five cores in terms of thickness of patterns. However, this study does not use the ideal methods outlined previously, to create such a model. This study is limited to core data, a small volume of outcrop data from one location, but no petrophysical logs or seismic data. Furthermore, the cores that were logged, the distance between some is extensive, with one well 160km from the next nearest well.

This chapter also addresses environments throughout deposition of the Eagle Ford Fmn (Figure 6.0). The distribution of high TOC, clay rich lithofacies present in the Lower Eagle Ford Fmn represents anoxic, marine conditions with sufficient sedimentation rates to preserve and bury organic material before the onset of OAE2. In contrast the Upper Eagle Ford Fmn records increasing ocean turnover, increased oxygenation of the water column, and decreasing sedimentation rates which equated to destruction of organic matter and production of carbonate during OEA2. This produces low TOC, clay-poor, carbonate dominated lithofacies containing bioturbation, high quantities of faunal species observed in the Upper Eagle Ford Fmn.
Figure 6.0. Generalised paleomap of the southern Western Interior Seaway (WIS) seabed, with sea level variation and physical and chemical processes. 

A. The WIS during the Late Cenomanian (99.6-94 Ma) where sea level is relatively low but transgressing. Organic carbon preservation is prevalent due to dense saline conditions.
Tethyan waters creating a stagnant, anoxic water column. Despite a stagnant water column, sufficient upwelling is able to bring enough nutrients to the photic zone for primary productivity. High preservation rates allows the majority of organic carbon to be preserved, despite initial productivity rates being relatively low. **B. The WIS during OEA2 at the C-T boundary and lower Turonian.** Sea level has risen due to transgression and is at its highest during the Cretaceous (sea level highstand). Fresh, boreal waters are drawn down the western side of the WIS and displace the dense, saline Tethyan waters, creating turnover increased upwelling and primary productivity. Water column turnover supplies oxygen to the bottom waters oxidising organic carbon. Despite higher levels of primary productivity in the surface waters, little of the organic material reaches the seafloor without being reduced. The ability of the basin to preserve organic matter is majorly weakened with carbonate the most common mineral precipitated at the seafloor. TOC is low.

### 6.2.2 Chapter 3: Diagenesis in the Eagle Ford Fmn

The second main chapter of this study (chapter 3) has identified which diagenetic reactions have taken place in the lithofacies of the Eagle Ford Fmn. Diagenesis has had a significant impact on the mineralogical and geochemical composition of the lithofacies. Diagenetic processes are interpreted to have occurred early in the Eagle Ford Fmn- immediately after deposition and during deposition in the case of the Upper Eagle Ford Fmn, as sediment and organic matter was in transit through the water column.

In the Lower Eagle Ford Fmn non-ferroan, calcite cements and framboidal pyrite infill planktonic foraminifera. Foraminifera infilling cements are interpreted to have occurred early during deposition. Kaolinite is also interpreted to have precipitated early via available Si through dissolution of biogenic Si tests and the organic acids mobilising Al from the decay of organic matter. Coccolith fragments constitute the bulk of the carbonate in the Lower Eagle Ford Fmn and have been mildly recrystallised at depth. Deep burial diagenetic processes are particularly prevalent in the Lower Eagle Ford Fmn. Smectite is fully converted to 70-80% mixed layer I/S providing ions such as Si, Fe and Al for the precipitation of authigenic quartz and chlorite. but products are still observed in the Upper Eagle Ford Fmn, such as the smectite to illite conversion reaction (Figure 6.1).

In contrast the Upper Eagle Ford is mainly impacted by early and syn-depositional processes. Aerobic oxidation of organic matter is interpreted to reduces TOC content in the Upper Eagle Ford Fmn. Further microbial processes precipitate extensive and pervasive non-ferroan, zoned, calcite cements which infill and surround biogenic
The presence of burrowing and a variety of fauna all suggest oxygenated marine conditions where organic matter is severely degraded. Due to the low TOC values it is interpreted aerobic oxidation of organic matter has occurred in these lithofacies, creating TOC lean mudstone and carbonate rocks. This is process is interpreted to be the very first process to occur and is likely to have occurred in the water column or at the sediment water interface. Burrowing present in the skeletal wackestones to packstones and the bioturbated mudstones to wackestones indicates stable, well oxygenated marine conditions where faunal communities can thrive within the sediment at the sediment water interface. Due to the lower TOC content in the Upper Eagle Ford Fmn, hydrocarbon expulsion is much less compared to the Lower Eagle Ford Fmn. The skeletal wackestones to packstones are the only lithofacies in the Upper Eagle Ford Fmn that can contain significant organic content and therefore, expel hydrocarbons. The bioturbated lime mudstones to wackestones and foraminiferal dominated packstones to grainstones are interpreted not to expel any hydrocarbons at all due to their low TOC content (~0.5%, see Table 3.1) and very high carbonate content (>90% see Table 3.1 and Figure 3.1). Carbonate cement content over 90% is likely to close any porosity in these lithofacies. If there are pockets of significant organic content capable of generating hydrocarbons, it is unlikely they would able to flow due to the low porosity closed up by carbonate cements (Figure 6.2).
6.2.3 Chapter 4: The origin of concretions and limestone beds in the Lower Eagle Ford Formation

The third main chapter of this study (chapter 4) addresses why concretions and laterally continuous limestone beds are present in the Lower Eagle Ford Fmn. Concretions are common features in the Lower Eagle Ford Fmn. They are distinctive in both outcrop and core due to their colour and hardness which make them protrude in outcrop. There are four types of concretion identified within the organic-rich weakly laminated mudstones (lithofacies 2) present in the west Texas outcrops (see chapter 4):

5. Type 1 is a continuous 20-30cm thick limestone bed that extends along the entire outcrop (>1km long). A volcanic ash bed (bentonite) is directly beneath the cemented bed.
6. Type 2 concretions are known as “footballs” as they resemble American Footballs in appearance. They are isolated and occur every ~5-10m above a volcanic ash bed and are surrounded by organic rich mudstone.

7. Type 3 concretions are lenticular, elliptical concretions that are no larger than 10cm thick, but vary in length. Some concretions are <50cm while others can be >1.5m long. Their y axis dimension and how far they extend into the outcrop is unknown. This type of concretion contains ripple laminae and cross trough stratification.

8. Type 4 concretions are a thin continuous bed of limestone (~10cm) similar to Type 1 but ‘pulse’ in localised areas to a thickness of ~30cm. They are thin, elongated, and elliptical in shape similar to Type 3 concretions; however they are connected by a thin strand of limestone that runs continuously throughout the outcrop. This type of concretion contains ripple laminae and cross trough stratification.

There are numerous mechanisms that have been interpreted to cause the different types of concretion. For the type 1 concretions is interpreted a volcanic event occurred during late transgression which was gradually reducing sediment supply. With additional skeletal material accumulating on the seabed and sediment starvation due to transgression and a possible high stand, a significant (30cm thick) carbonate bed was precipitated throughout the Eagle Ford Fmn basin. The type 4 concretions are interpreted to have formed in similar conditions but without a significant reduction in sediment supply, which resulted in the formation of a thinner carbonate bed with distinctive sedimentary structures.

The type 3 concretions are interpreted to be formed syn-deposition and present on the seafloor. They are interpreted to be driven by high frequency sea-level variation that reduced sediment supply to the basin. Sporadic deposition of sediment left certain areas of the seafloor exposed allowing for microbial redox reactions to oxidise organic matter and precipitate carbonate. Like the type 4 concretions bottom water currents re-distributed sediment creating the sedimentary structures observed in outcrop but allowing the formation of lenticular, discontinuous concretions across a stratigraphic horizon.

The origin of the type 2 concretions is interpreted to be sulphate-reducing bacteria producing exopolymeric substances (EPS), which have colonised local areas of the lithology influencing the morphology, mineralogy and precipitation of carbonate. Local communities of EPS creating lithifying microbial mats are interpreted to have precipitated the type 2 concretions within the surrounding organic-rich weakly laminated mudstones in
where the environment was ideal for source rock deposition. The effects of a bentonite bed underlying the type 2 concretions (and organic-rich weakly laminated mudstones), remains unclear.

This chapter highlights the number of factors that have affected the diagenesis of the Lower Eagle Ford Fmn. Numerous complex interactions control the formation of organic-rich mudstone, concretions and continuous limestone beds within the Lower Eagle Ford Fmn. Overall, this chapter has shown how diagenesis can be highly variable within a small stratigraphic section (10m of outcrop). The features discussed in this chapter (organic rich mudstones and Types 1, 2, 3 and 4 concretions) have all been influenced by diagenesis, but by varying degrees and by some processes more than others. The Type 2 concretions are the only features that are purely diagenetic. The other concretions (Types 1, 3 and 4) and the organic-rich mudstones are primarily diagenetic. However, marine carbonate input, sediment input, sea level variation, primary productivity and tectonic/volcanic activity are all primary factors that have had an effect on the diagenetic processes that took place in the formation. All of the factors mentioned above bare an effect on carbonate precipitation in the Lower Eagle Ford Fmn and organic matter preservation, with a change of oxygen content in the water column not necessary for the precipitation of carbonate concretions within the organic-rich mudstones and/or the destruction of organic matter within the concretions.

This chapter also highlights that; while petrographic studies are highly valuable because they can help identify specific processes that have created particular mineral compositions, textures and physical properties such as porosity and permeability. This chapter highlights the need to incorporate all levels of investigation from the micro-scale to basin scale to fully understand how organic-rich formations like the Eagle Ford Fmn are deposited and buried.

6.2.4 Chapter 5: Porosity Distribution in the Eagle Ford Formation

The fourth main chapter of this study (chapter 5) addresses how porosity types and their distribution between the lithofacies vary. It also discusses how porosity distribution effects total porosity and where the best areas of the Eagle Ford Fmn (“sweetspots”) are to target for stimulation and production.
Mineralogy, organic content and thermal maturity are the main drivers of porosity distribution. The Lower Eagle Ford Fmn contains the highest total porosities. However the vast majority of this porosity is observed as clay-held nano porosity. The carbonate rich lithofacies which contain less organic matter, have a different porosity distribution. Intra-crystalline porosity within carbonate cements dominate the porosity distribution with pores an order of magnitude (>1µm) larger compared to the organic rich, clay rich lithfacies. In this study, samples were analysis were relatively immature (~0.9Ro%) resulting in little secondary organic-porosity observed within organic matter. Therefore areas of the Eagle Ford Fmn consisting of carbonate rich lithologies (lithofacies 3, 5, 6 and 7) may be the better units to aim for hydraulic stimulation if exploration and production companies own acreage in relatively thermally immature areas. Clay-hosted nano-porosity is unlikely to produce any permeability or significant porosity connectivity and permeability. Only larger, secondary porosity developed through thermal maturity within the organic matter (intrabitumen) is likely to produce significant storage for free hydrocarbons.

6.3 Synthesis - impacts on reservoir properties

6.3.1 Reservoir properties in the Lower Eagle Ford Fmn

Diagenetic reactions are one of the main drivers of mineralogical and geochemical composition, and therefore lithofacies variation observed the Eagle Ford Fmn. Previous authors have also concluded that diagenetic reactions in marine derived mudstones are often the processes that have the biggest influence on the composition of a source rock/mudstone (Claypool, 1974, Curtis, 1977, Irwin, 1977, Coleman, 1985, Taylor, 2010, Macquaker et al., 2014). Along with mineralogical and geochemical composition, diagenetic processes also have a large impact on physical properties, such as strength, brittleness, porosity and permeability (Aplin, 2000, Aplin and Macquaker, 2011, Aplin and Taylor, 2013, Yang and Aplin, 2009). Primary factors such as sea level variation, sediment input and tectonic are also a main driver or lithofacies distribution.

The Lower Eagle Ford Fmn mainly comprises of clay-rich lithofacies (Figure 6.2 and 6.3), which contain high quantities of TOC (4-8%), a high quantity of authigenic clay minerals and lower quantity of authigenic carbonate cements. Anaerobic conditions during deposition and
Figure 6.2. Comparison of the primary and diagenetic processes that have created the distinctive organic, clay–rich Lower Eagle Ford Fmn and the organic-poor, carbonate-rich Upper Eagle Fmn. Lower Eagle Ford resulted from anaerobic conditions, low sea level, low ocean turnover and higher siliciclastic input, clay diagenesis and hydrocarbon.
expulsion. Meanwhile the Upper Eagle Ford Fmn resulted from aerobic conditions, higher sea level, ocean turnover and lower siliciclastic input, extensive carbonate precipitation and recrystallisation and no hydrocarbon expulsion. Variations in diagenesis create the physical and chemical properties of the lithofacies within the Eagle Ford Fmn. Early carbonate cementation of foraminifera, clay diagenesis and hydrocarbon expulsion are the main diagenetic reactions in the Lower Eagle Ford. In the Upper Eagle Ford Fmn, extensive carbonate precipitation dominates creating a heavily cemented, TOC-poor section. These processes create a TOC-rich, clay-rich Lower Eagle Ford ideal for targeting if maturation is >1.5\textit{Ro}%. The Upper Eagle Ford Fmn is too heavily cemented with porosity ~3% and with no hydrocarbons present is unsuitable for targeting. The Middle Eagle Ford Fmn however, is ideal for targeting in maturity is <1 \textit{Ro}% because intercrystalline porosity is present allowing for the storage of free hydrocarbons.

early burial are interpreted for the preservation of organic carbon, with only some degradation occurring through anaerobic microbial induced redox reactions (Figure 6.2) (Tyson, 2005, Pederson and Calvert, 1990, Wignall, 1994, Donovan et al., 2012). The Lower Eagle Ford Fmn is therefore regarded as a first class source rock due to its organic content and hydrocarbons it has already produced (Driskell et al., 2012, Liro et al., 1994, Donovan et al., 2012, Denne et al., 2014).

High quantities of detrital smectite were present in in Lower Eagle Ford Fmn, which are converted to mixed layer I/S and illite. Kaolinite and chlorite are also common, along with authigenic quartz cements, with all more prominent in the more clay-rich lithofacies (1 and 2). Clay mineral precipitation has a major impact on reservoir properties as they have significantly reduced porosity in the Lower Eagle Ford Fmn by precipitating within primary and secondary porosity (Figure 6.2). A significant quantity of the porosity in the Lower Eagle Ford Fmn is observed as clay mineral-hosted porosity, followed my organic matter-held porosity. Pores sizes are mainly 50-100nm in size. Although these lithofacies contain the highest total porosity figures (see Chapter 5) other studies have shown (Fishman et al., 2013a, Fishman et al., 2013b), they contain significantly less permeability compared to other lithofacies which contain less clay minerals. Organic porosity is known to contribute to porosity and gas storage, however both are a function of thermal maturity and are only significant in areas with maturities >1.5\textit{Ro}%. (Pommer et al., 2014, Rine et al., 2013). This study (Chapter 5) was completed using samples at 0.9\textit{Ro}%, therefore little secondary porosity was observed within the organic matter (porosity created due to mass loss in kerogen through
maturation, generation and expulsion of hydrocarbons). Hence, organic porosity has less of an impact on porosity distribution compared to clay mineral-held porosity (see Chapter 5).

High quantities of clay minerals have effects on rock mechanics and the rocks ability to “hydraulically fracture” (King and Corporation, 2010, Rahm, 2011, Davies et al., 2012). Although the Lower Eagle Ford Fmn is mainly a calcareous unit, high clay content can make the Lower Eagle Ford Fmn less favourable for stimulation due to reduced brittleness (Aplin and Macquaker, 2011, Aplin et al., 2006). Little is understood how clay minerals behave when they are subjected to high quantities of fluid during stimulation (Arugundade and Sohrabi, 2012, Martin et al., 2011). It is thought clay minerals may swell and close the remaining porosity and the fractures created by the stimulation in the formation (Jones, 1964, Arugundade and Sohrabi, 2012). A clay mineral swelling process is likely to have a significant decrease in well performance over a short period of time (Arugundade and Sohrabi, 2012, Martin et al., 2011).

6.3.2 Reservoir properties in the Middle Eagle Ford Fmn

Transitioning into the Upper Eagle Ford Fmn (see Chapter 1), clay diagenesis has less of an impact on reservoir properties due to an overall decrease in clay content. Instead carbonate diagenesis has more of an impact on rock physical and chemical properties. This is highlighted in XRD as calcite content increases with clay content decreasing and in thin section as carbonate cements infill, over grow and surround biogenic debris. Here the lithofacies present (Figure 6.2) are mainly the laminated foraminiferal rich wackestones, skeletal wackestone to packstones and bioturbated lime mudstones to wackestones, which are all carbonate-rich, with some significant organic content (2-4%). A significant quantity of the carbonate is diagenetic which has precipitated early and often overprints the original composition. In some cases, such as the bioturbated lime mudstones to wackestones, recrystallisation has occurred. Carbonate cements have infilled all of the primary porosity, significantly reducing total porosity (see Chapter 5). Total porosities are lower compared to the clay/organic-rich lithofacies observed in the Lower Eagle Ford Fmn. However, porosity distribution differs compared to the organic/clay-rich lithofacies where the majority of pores are much larger and observed as intra-crystalline pores within carbonate cements. Fishman et al., 2013a, show that lithofacies containing high carbonate content with a pore network consisting of 1.5-5µm pores produce
permeability’s in order of magnitude larger than the organic/clay-rich lithofacies (see Chapter 5).

With a decrease in clay mineral diagenesis, the inter-crystalline pore network is less likely to be infilled with precipitating silicate minerals during later diagenesis, allowing for larger intra-crystalline pores to remain open and store free hydrocarbons (Pommer et al., 2014, Fishman et al., 2013a, Fishman et al., 2013b). Inter-crystalline pores are much larger compared to nano-organic or clay-held porosity and are likely to produce significant porosity that allows fluids to flow (Fishman et al., 2013a, Fishman et al., 2013b). With an increase in carbonate content, the carbonate-rich lithofacies are more brittle and are more likely to propagate fractures further away from the well-head (King and Corporation, 2010, Davies et al., 2012).

Figure 6.3. Summary of target zones for hydraulic stimulation in the Eagle Ford Fmn. The Lower Eagle Ford Fmn. The transition of Lower to Upper Eagle Ford Fmn. The Upper Eagle Ford Fmn. The three zones are based on mineralogy, diagenetic processes, TOC (wt%), total porosity (φ) and pore type distribution. Due to the overall carbonate content throughout the Eagle Ford Fmn, it is ideal for hydraulic stimulation. However organic content, mineralogy and maturity have a large impact on free gas storage.
Due to a decrease in clay mineral content, the impact of clay mineral swelling from frac fluids within artificial fractures is likely to be reduced, allowing for more consistent flow back rates over time (Arugundade and Sohrabi, 2012, Martin et al., 2011, Davies et al., 2012). The middle part of the Eagle Ford Fmn where the Lower Fmn transitions into the Upper may therefore be the optimum area to target due to its organic content, storage and flow capability and fracability if maturity is < 1% Ro (Figures 6.2 and 6.3).

### 6.3.3 Reservoir properties in the Upper Eagle Ford Fmn

Carbonate diagenesis dominates the Upper Eagle Ford Fmn. Early diagenetic processes have precipitated extensive quantities of carbonate, with 85-90% carbonate rock composition calcite along with small quantities of quartz and mixed layer I/S. Fully oxic depositional conditions are interpreted for this section of the formation due to the lack of organic content and the presence of burrowing in core. (Al Balushi et al., 2013, Tyson, 2005). Carbonate precipitation and cementation is extensive leaving total porosities <3%. With less porosity and little to no organic material present, the Upper Eagle Ford Fmn is of little interest to exploration and production companies.

Overall, the Lower Eagle Ford Fmn and the “middle” Eagle Ford Fmn are the two optimum areas of the Eagle Ford Fmn to target for hydrocarbon extraction depending on maturation and local stratigraphy (Figure 6.1 and 6.2). The Lower Eagle Ford is the most organic-rich and is likely to contain the highest quantities of hydrocarbons compared to other areas of the Eagle Ford Fmn overall (Wignall, 1994, Donovan et al., 2012, Liro et al., 1994). However this does not necessarily mean this part of the stratigraphy is the optimum target area of the formation. Maturity has a significant impact. In samples below 1.5 Ro% there is minimal secondary organic-porosity development within the organic matter. The majority of porosity present in thermally immature samples is meso-scale clay-held porosity (see chapter 5) and there are uncertainties whether clay minerals create permeability. Their behaviour and ability to swell when introduced to high volumes of fluids are also an issue making it less of an attractive area of stratigraphy to target (Arugundade and Sohrabi, 2012).
The Lower Eagle Ford Fmn can also be truncated in certain geographical locations of the formation leaving little area of the organic-rich section to target. The area which transitions from the Lower Eagle Ford Fmn to the Upper Eagle Ford Fmn (Figure 6.2), contains significant TOC, however has withholds inter-crystalline porosity with larger pores and higher permeability’s (chapter 5). In areas of the Eagle Ford Fmn where the organic-rich Lower Eagle Ford is truncated and/or below a maturity of 1.5 Ro% the transition area of Lower to Upper Eagle Ford Fmn containing significant inter-crystalline porosity may be the best area of the formation to target for hydrocarbon stimulation and production (Figure 6.1 and 6.2).

6.4 Future work

To better understand diagenesis in the Eagle Ford Fmn and the impacts diagenesis has on reservoir properties, further research could focus on:

The precipitation of quartz cements is still poorly understood in the Eagle Ford Fmn. Observations via scanning electron microscopy suggests the vast majority of quartz is authigenic cement. However, without a SEM with a cathodoluminescence capability it is impossible to determine, hence SEM-CL is not present in this study. Future analysis with a CL-SEM will confirm if quartz cements are authigenic or of detrital origin. This will help future researchers understand silica mobilisation and availability in pore fluids at depth.

The elemental composition of carbonate (calcite) cements is poorly understood. From CL we observe cements are non-ferroan with some cements containing a smaller ratio of iron/manganese due to luminescence variations. However there is a lack of quantification of these elements. Micro-probe analysis would confirm iron and manganese content within the carbonate cements and would supplement CL observations. It would also help researchers understand the diagenetic processes involving iron and manganese.

Bulk isotopic compositions are a good analytical technique for identifying a carbonates source. However bulk techniques are limited to entire carbonate assemblages and become problematic when there are multiple phases/sources of carbonate precipitation. This results in mixed isotopic signatures which are problematic to base interpretations. Utilising the relatively new technological advancement of Nano – Secondary Ion Mass Spectrometry (NANO-SIM)
Ion-probe analysis for isotopic compositions, will allow future researchers to obtain the isotopic compositions of carbonate from a specific area of interest.

For example, focusing on the isotopic composition of calcite cement within a foraminifera chamber, thus the composition not being skewed by the marine derived carbonate (coccolith debris) surrounding the chamber. Utilising NANO-SIM technology would help constrain whether carbonate in the lithofacies heavily comprised of calcite cements is fully authigenic or recrystallised marine carbonate. The same techniques could be used to improve the accuracy of carbonate isotopic compositions in the concretions, especially the type 1 and type 4 concretions, which contain a significant quantity of marine derived carbonate (coccolith debris) within the micritic matrix.

This study used cores available from the Bureau of Economic Geology (BEG) in Austin Texas. Cores are from various locations of the Eagle Ford Fmn and are too far from one another for stratigraphical correlation. This makes sequence stratigraphy impossible. Ideally if further cores were available for analysis a full sequence stratigraphic framework could be created. This would confine concretion and bentonite bed continuation observed in outcrop and would help other better understand the high thickness variability of the formation observed by many researchers working in operating companies.

To further enhance the understanding of diagenesis in the Eagle Ford Fmn, a maturity transect study would be ideal to help understand physical rock properties as organic and inorganic minerals get further buried. A particular focus on organic matter and organic-porosity evolution would be an interesting study to help understand overall porosity and permeability compared to porosity observed as inter-crystalline porosity, which is unlikely to change throughout burial.
7. References


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7. Appendix
7.1 Data – thin sections analysed

Shell J A Leppard 1-H

Shell Hay E-D 1

H-P Orts 2

Lloyd Hurt 1

Wagner Bros Inc 11

J W Bretchell

J W Blumberg

Matthews J L 1-1

7.2 Well logs and tabulated data locations
Matthews J L 1-1

Strat Depth(ft.) Lithofacies Features 3rd order 4th order 5th order

Well Name: Matthews J L 1-1

GPS Location

<table>
<thead>
<tr>
<th>Latitude</th>
<th>Longitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.263</td>
<td>-100.302b</td>
</tr>
</tbody>
</table>

Thin section location(h)
4650.3-4661.1
4670.1-4670.5
4671.9-4671.2
4673.4-4673.8
4673.5-4673.7
4673.5-4676.5

XRD sample location(h)
4660.5-4661.1
4670.1-4671.8
4671.0-4672.2
4672.1-4672.5
4673.5-4673.7
4676.5-4676.5

Rock Eval sample location
4673.5

Key
- Thin section and XRD sample location
- Rock Eval sample location
- Photograph

266
J W Blumberg

Well Name: J.W. Blumberg
GPS Location:
Lat: 29.3797
Lon: -98.8623

<table>
<thead>
<tr>
<th>Thin Section location (ft)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4177.5-4178.7</td>
</tr>
<tr>
<td>4190.7-4191.1</td>
</tr>
<tr>
<td>4211.1-4211.7</td>
</tr>
<tr>
<td>4211.1-4211.1</td>
</tr>
<tr>
<td>4221.6-4223.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>XRD sample location (ft)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4178.5</td>
</tr>
<tr>
<td>4190.6</td>
</tr>
<tr>
<td>4211.2</td>
</tr>
<tr>
<td>4211.2</td>
</tr>
<tr>
<td>4223.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
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<th>Rock Eval location (ft)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4211.9</td>
</tr>
<tr>
<td>4213.7</td>
</tr>
<tr>
<td>4216.9</td>
</tr>
</tbody>
</table>

Key:
→ Thin section and XRD sample location
→ Rock Eval sample location
☑ Photograph
W Bretelll

Strat

Austin Chalk

Upper Eagle Ford

Buca

Depth (ft)

Lithofacies

Features

3rd order

4th order

5th order

Well Name

GPS Location

W.Bretelll

Latitude

Longitude

29.3015

-98.0220

Thin Section location (ft)

3254.7
3270.6
3296.9
3300.1
3303.8
3304.6
3312.2
3312.4
3312.7
3312.9

XRD sample location (ft)

3254.7
3270.5
3300.9
3303.9
3312.0
3312.2
3312.8
3314.7
3315.7

Rock Eval location (ft)

3254.6
3270.4
3315.7

Key

→ Thin section and XRD sample location

→ Rock Eval sample location

□ Photograph
7.3 Figure of wells to a comparable scale
Diagenetic Evolution of The Eagle Ford Formation, SW Texas: Impacts upon Reservoir Quality and Rock Properties

Richard.T. McAllister*, University of Manchester; Kevin.G. Taylor, University of Manchester; Beatriz Garcia-Fresca, Statoil Gulf Services, Houston, Texas, USA

Abstract

The Eagle Ford Fm in southwest Texas is a self-sourced oil and gas reservoir currently stimulated through hydraulic fracturing to produce economic quantities of hydrocarbons. Both early and burial diagenesis has had a major impact upon the rocks and their resulting reservoir quality. In this presentation we infer mineral reactions and precipitation that took place during diagenesis through a combination of mineralogical and petrographic analysis using XRD, optical and electron microscopy. We highlight how such an understanding can improve prediction of rock properties and reservoir quality.

Along with compaction and de-watering, we infer that bacterial sulphate reduction had a major impact during early diagenesis as it resulted in significant calcite cement precipitation. Calcite cements infill bioclasts and foraminifera chambers, thereby significantly reducing intra-granular porosity. Fine grained calcite cements the matrix and coccolith fragments that resulted in reduction in inter-granular porosity and its interlocking texture will likely lead to an increase in rock brittleness. Optical microscopy and cathodoluminescence (CL) highlight the extensive and invasive calcite precipitation that occurs within concretional features in the Eagle Ford Fm. Zonation within the calcite cements suggests evolution in pore water chemistry and this is interpreted to be caused by changes in microbial organic matter oxidation.

Foraminifera chambers are commonly infilled with kaolinite, as well as or instead of calcite. There is no clear petrographic evidence to suggest which came first, but based on the fact the foraminifera are not compacted we infer early diageneric origin. Unlike the calcite infills, kaolinite infills preserve significant inter-crystalline porosity. Authigenic kaolinite is also present as multiple crystal grains within the matrix, and replacing 30-60µm detrital grains- which we infer to be feldspars.

During late burial, authigenic quartz cement commonly precipitated around detrital quartz grains and calcite cements, further reducing inter-particle and inter-crystalline porosity. This source of this silica may have been clay mineral reactions or biogenic silica dissolution. Chlorite is present in the form of 5-15µm wispy flakes in the most thermally mature samples. The precipitation of clay minerals during deeper burial leads likely to a decrease in rock brittleness and a further reduction in micro-porosity in the matrix.
Key Words: Diagenesis, Eagle Ford Fm, porosity.

Introduction

Our understanding of fine grained sedimentary rocks has significantly progressed since these rocks became a target for oil and gas production (Donovan et al., 2012, Wignall, 1994, Macquaker et al., 2014). Our advances in understanding has shown that fine grained sedimentary rocks (more commonly called mudstones, which are mainly composed of material <62.5µm), are highly variable in composition, texture and fabrics. These variations can be seen in every scale, from outcrop (although sometimes difficult) to the nanometre. In unprepared hand specimens and in outcrop, mudstones from different locations often look similar. But in well prepared core and at higher magnifications using thin sections, mudstones are highly heterogeneous (Taylor and Macquaker, 2014). Detrital sand, silt, clay, organic matter (OM) and authigenic minerals from diagenetic processes, all influence the composition, texture and microfabric of a fine grained sedimentary rock (Macquaker et al., 2014, Taylor and Macquaker, 2014).

Diagenesis plays a large and important role within mudstones (Batchurst, 1974, Macquaker and Adams, 2003, Reinhard, 1986). Unlike other sedimentary rocks, pre-lithification diagenesis (mainly involving organic matter and microbial induced redox reactions), have a large impact on the final composition of a mudstone. In mudstones early diagenetic processes control organic carbon burial and ultimately TOC content of source rocks (Taylor et al., 2010, Taylor and Macquaker, 2014, Aplin and Macquaker, 2011, Macquaker et al., 2014, Al Balushi et al., 2013). Bacterial mediated reactions dominate pre-burial diagenesis with the oxidation of organic matter, the reduction of sulphate and iron being the most common processes and they produce carbonate, along with other minor minerals (Irwin, 1977, Curtis, 1977, Macquaker et al., 1997, Singleton et al., 2002, Taylor et al., 2010). The precipitation of carbonate helps retard the lithification of sediments and initially preserves primary porosity during burial (Heydari and Wade, 2002, Hentz and Ruppel, 2010). Equilibrium driven diffusion reactions dominate deeper burial diagenesis where silicate cements and clay minerals precipitate at higher temperatures and pressures infilling primary and secondary porosity and ensures low porosity and permeability’s in mudstones (Laubach et al., 2010, Curtis, 1977, Macquaker et al., 1997).

The aim of the research presented here is to look at the composition, and diagenetic fabrics and textures present within two distinct lithofacies within the Cretaceous Eagle Ford Fm, South Texas. We will focus on their sedimentologocal and mineralogical composition, paragenetic history and how this affects porosity types and their distribution.

The Eagle Ford Formation, South Texas

The late Cretaceous (Cenomanian-Turonian) Eagle Ford Fm is a self-sourced oil and gas reservoir currently being targeted for economic quantities of hydrocarbons through hydraulic stimulation. Despite being extensively drilled for hydraulically fractured hydrocarbons in the last five years the overall geology of the Eagle Ford formation is poorly understood (Dawson, 1997, Dawson and Almon, 2010, Aragundade and Sohrabi, 2012). The Eagle Ford Fm is an organic rich marl, originating from pelagic and hemipelagic environments found within the Western Interior Seaway. The Eagle Ford Fm is split into two distinct sections; lower Eagle Ford and upper Eagle Ford. The lower Eagle Ford is a carbonate rich (40-90% CaCO₃) source rock with TOC% values of ~6% and HI of ~500mgHC, while the upper section is less organically rich (2-3% TOC) with higher carbonate content (50-100%) (Liro et al., 1994, Hsu and Nelson, 2002a, Dawson and Almon, 2010).

Methods

Observations in outcrop and core were studied in west of Cumstock, along Highway 90, Texas, and the Bureau of Economic Geology (BEG) in Austin, Texas, respectively. A total of seven cores (HP Orts #2, Shell Leppard #1, E.D Hay Unit #1, Wagner Bros, Zavala Matthews #1, J Blumberg, Lloyd Hurt #1), were observed from the BEG with 45 samples extracted from the cores for petrological, mineralogical and geochemical analysis along with 12 samples from outcrops situated along US. Highway 90. All samples were cut and prepared (and analysed geochemically) at Statoil ASA, Bergen, Norway. An additional 32 thin sections supplied from Statoil...
ASA were also analysed using standard petrographic techniques. Macroscopic, microscopic and mineralogical analysis was undertaken at the University of Manchester, UK.

Macroscopic (polarised light microscopy and cathodoluminescence, CL) and electron microscopic (Scanning Electron Microscopy, SEM) observations form the base of this study complemented with mineralogical data (X-ray Diffraction, XRD), geochemical data (Rock Eval pyrolysis) and the porosity of selected samples was determined on core plugs of samples using standard helium porosimetry. 77 thin sections cut at 20µm and highly polished for analysis under polarised light and CL to identify grains, deposition texture and carbonate cements. Further analysis to identify the origin, porosity and matrix texture of micro grains was carried out on a Philips XL30 ESEM-FEG fitted with an EDAX Genesis EDS system. Backscattered electron images were obtained under high vacuum mode with an accelerating voltage of 15kV.

Results

I. Facies Type

Seven distinct lithofacies were identified from outcrop, core, thin section and electron microscopy (Fig 1). The lithofacies are characterised by: grain type, grain size, texture, colour, sedimentary structures biogenic content and diagenetic features. For this study only two lithofacies will be studied in detail. A full lithofacies study is part of a separate piece of work. Table 1 provides a summary of each lithofacies. In this manuscript only two will be described in detail. These two were chosen as they represent extremes in organic matter/clay and carbonate content.

1. Weakly Laminated Foraminiferal Mudstone

The weakly laminated foraminiferal mudstones are present mainly in the lower Eagle Ford (Fig 1). The weakly laminated foraminiferal mudstones are black in colour with some sections, especially in cores from the northeast of the formation, having a brownish-black colour. This facies comprises mainly of calcite, clay minerals and quartz. XRD shows that the bulk component of the weakly laminated foraminiferal mudstones is calcite (average 52%). Clay minerals constitute on average 30%, quartz 12% and plagioclase and K-feldspar (3.1% and 1.8% respectively). Clay XRD shows clay mineral composition, smectite (average 16%), illite (average 10%) and kaolinite (average 4%). The laminated foraminiferal mudstones are the most organic rich. TOC values are range from 6-8%.

Planktonic foraminifera are common and are the main silt sized (>62.5µm) component along with fragmented inoceramids bivalves. Both are found mainly in sub millimeter to millimeter scale planar laminae (Fig 1). Some laminae are truncated or contain wavy ripples, although the latter are rare. Black pyrite framboïds are less common but are always present in thin section. Phosphatic fish bones and teeth are present in some samples.

Thin section analysis through plane polarised light shows the accumulation of planktonic foraminifera along traction laminae. The foraminifera are well sorted with the majority infilled with calcite cement, whilst some foraminifera chambers are infilled with kaolinite. Cathodoluminescence (CL) indicates calcite is non-ferroan and contains no zoning (Fig 1). Electron microscopy highlights the micro-crystalline (2-5µm), plate-like carbonate that constitutes the bulk of the matrix. These plates are coccolith fragments that lie in random orientation among the clay minerals (0.06µm-62.5µm) (Fig 1). The coccolith fragments appear to form the bulk of the calcite seen in XRD. At high magnification wisps of smectite and illite can be seen within the matrix along with kaolinite. Larger, replacive kaolinite grains are seen within the matrix. These grains look to have replaced detrital silt sized feldspars. Finely grained authigenic quartz is present within the matrix of the weakly laminated foraminiferal mudstones. Authigenic quartz is common and is seen attached to foraminifera and carbonate cement grains. Bitumen is common within foraminifera and the matrix. Bitumen infills the small amount of porosity left, usually between clay minerals and coccolith fragments.
<table>
<thead>
<tr>
<th>Facies</th>
<th>Main minerology (XRD) % (average)</th>
<th>Colour</th>
<th>Main Grains Present</th>
<th>Sedimentological Characteristics</th>
<th>TOC %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>Quartz</td>
<td>Clays</td>
<td>Black to very dark grey-green</td>
<td>Planktonic Foraminifera</td>
<td>Faintly laminated- sometimes massive. Burrowing</td>
</tr>
<tr>
<td>1 Argillaceous Mudstone</td>
<td>29</td>
<td>22</td>
<td>44</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 Weakly laminated Foraminiferal Mudstone</td>
<td>47</td>
<td>18</td>
<td>27</td>
<td>Black perfume of Foraminifera. Fragments of Inoceramid biovalves.</td>
<td>6-8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ripple laminae. Most are planar but truncated is common. Some are wavey but are only present at the bottom of packages where there is either a sharp or erosive contact. Burrows present but rare</td>
<td></td>
</tr>
<tr>
<td>3 Laminated Foraminifera rich Wackstone</td>
<td>62</td>
<td>15</td>
<td>14</td>
<td>Medium to dark Grey</td>
<td>4-6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Globigerinid Foraminifera.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Planar laminae. Some laminae resemble ripples, although this is rare. Burrowing is present</td>
<td></td>
</tr>
<tr>
<td>4 Lime Wackstone</td>
<td>90</td>
<td>5</td>
<td>5</td>
<td>Light Grey</td>
<td>1-3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Bivalves, and unidentifiable skeletal material</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Biotubated. Cemented with calcium carbonate. Fractures are infilled and closed with carbonate.</td>
<td></td>
</tr>
<tr>
<td>5 Skeletal Wackstone to Packstone</td>
<td>73</td>
<td>8</td>
<td>12</td>
<td>Medium to light grey</td>
<td>1-3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Fragmented Inoceramid bivalves, Globigerinid Foraminifera, Peloids, phosphate grains.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Strongly laminated and bedded. Scour and truncated surfaces in laminae and beds are common.</td>
<td></td>
</tr>
<tr>
<td>6 Foraminiferal dominated Packstone to Grainstone</td>
<td>84</td>
<td>7</td>
<td>8</td>
<td>Light grey</td>
<td>0.3-0.5</td>
</tr>
<tr>
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<td>Plantonic foraminifera, unidentifiable skeletal material</td>
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<td>Recrystallised. Fractures are infilled with calcium carbonate. Commonly interbedded with skeletal wackstones and packstones.</td>
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<tr>
<td>7 Bioturbated Bentonite (Volcanic Ash)</td>
<td>22</td>
<td>4</td>
<td>59</td>
<td>Green-grey-yellow</td>
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<td>Bioclasts, large skeletal fragments and teeth.</td>
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<td>Commonly massive, although some beds do contain planar laminae. Heavily bioturbated.</td>
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Table 1: Summary of the Eagle Ford lithologies present within the samples studied showing mineralogical composition, colour, sedimentological characteristics and total organic carbon (TOC). For this paper only two lithofacies will be described in detail; the Weakly Laminated Foraminiferal Mudstones and Lime Wackstone.
2. Lime Wackstone

The lime wackstones are distinctive and easy to identify in core due to their light-grey to grey colour compared to the dark organic rich ithofacies (Fig 1). Extensive cementation produces a homogenised looking lithofacies that varies little in colour and composition. No sedimentary structures are present except for erosive contacts at the top of some units. Foraminifera are difficult to spot due to the lack of contrast, but with a hand lens the larger specimens can be seen among the calcareous matrix. The lime wackstones are mainly found in the middle upper Eagle Ford Fm.

Thin section analysis reveals that the lime wackstones contain fragmented and recrystallised benthic and planktonic foraminifera and calcified radiolarians. Bivalve and echinoid fragments along with calcispheres are also common. All biota have been preserved to a degree by the infilling and/or replacement of calcite. CL indicates that the calcite is non-ferroan. Electron microscopy highlights the micritic nature of the matrix (3-7µm crystal sizes) found between the larger calcite cement grains. Coccolith fragments are less abundant in this facies. Clay and organic matter content is much less that in the weakly laminated foraminiferal mudstones and is seen in small quantities within the micritic matrix. Bitumen is present between isopachous cement grains in the lime wackstones but is much less common than the weakly laminated foraminiferal mudstones.

XRD shows the lime wackstones to be a carbonate rich lithofacies. Calcite content are on average ~83%, clays ~6%, quartz ~10%, plagioclase ~1.3% and K-feldspar 0.7%. TOC values for this facies are low compared to the weakly laminated foraminiferal mudstones with average values less than 1%.

II. Diagenetic textures

1. Weakly Laminated Foraminiferal Mudstones

The location, volume and fabric of the carbonate cements within foraminifera chambers indicate that they were precipitated prior to significant compaction- allowing the foraminifera to survive the pressures of later burial (Fig 1). Pyrite frambooids are present within foraminifera chambers adjacent to calcite cements. Pyrite frambooids are also common in association with calcite cements in polarised light and SEM. CL shows foraminifera to contain non zoned, non-ferroan calcite cements that are brighter than the original shell material (foraminifera chambers and shell fragments). Some foraminifera’s are infilled with kaolinite suggesting the precipitation kaolinite was an early diagenetic process.

The precipitation of authigenic quartz is a late diagenetic process. At higher magnifications quartz is seen infilling pore space between coccolith fragments (Fig 1). The release of Si from clay minerals reactions, or the transformation of biogenic silica tests are the likely sources of quartz cement. Kaolinite is present as both micron-sized crystals within the matrix and replacing silt sized detrital feldspars. Chlorite was the last mineral to be precipitated within the Eagle Ford Fm and has had a significant impact through porosity reduction. The expulsion of bitumen during late diagenesis infills the small amount of primary porosity left between coccolith fragments and clay minerals grains. In this particular sample (Fig 1) with a maturity of 1.1Ro%, some organic matter pores are visible within the bitumen, probably as a result of oil and gas of bitumen maturation and oil and gas expulsion.

1. Lime Wackstones

The precipitation of extensive calcite cement overprints the lime wackstones (Fig 1). Thin section analysis and CL indicate a high quantity of the calcite was precipitated in one early phase near the sediment water interface. The carbonate in this lithofacies is likely to have two sources; marine waters and via microbially induced reactions (OM oxidation and sulphate reduction). The carbonate cements display zonation indicating changes in pore water chemistry (iron and manganese content) as the cements precipitated during burial (Fig 1). The calcification of radiolarians indicates their silica content has been replaced by calcite early in diagenesis releasing free Si into the surrounding pore waters.
This is an example of a 3-D Subsurface Chart imported from Microsoft Excel. Left click on Insert on the menu bar and then select Object. You can either embed an existing file, or create your object at that point. You can also select to embed a Picture instead of an object.
Figure 1: A. Thin section micrograph of a weakly laminated foraminiferal mudstone illustrating sub-mm scale ripples, organic rich mud drapes (yellow arrow), planktonic foraminifera (Fm) infilled with calcite cement. Fecal pellets (green arrow) are aligned with laminae and contain randomly oriented calcite and clay mineral grains. Inoceramid fragments replaced by calcite are also a common feature in the weakly laminated foraminiferal mudstones. Scale bar 500µm. B. Thin section micrograph of a lime wackstone illustrating the extent of cementation overprinting the original matrix (Mtx). Benthic foraminifera are present in the lime wackstones and are usually fragmented, infilled and surrounded by calcite cement (C). Calcified radiolarians (Rd) are common in the lime wackestones. Scale bar 500µm. C. Thin section micrograph, identical image of A above but in CL showing the dull, non-ferroan calcite cement within the matrix of the weakly laminated foraminiferal mudstone. Foraminifera’s (green circle) and fecal pellets (yellow arrow) contain brighter luminescing cement compared to the rest of the matrix, suggesting earlier infill of cement when iron was sequestered into pyrite via sulphate reduction Scale bar 500µm. D. Thin section micrograph, identical image of B above in CL showing dull, non ferroan calcite cement (C), that overprints the lime wackstones. Zoning in the cements (green circle) is common in the lime wackstones indicating a change in pore water chemistry as the cement is precipitated. Sulphate reducing bacteria near the surface initially produce calcite cements with a brighter luminescence but with burial the cements ‘dull’ as sulphate reduction reduces allowing iron to be sequestered into the cements. Scale bar 500µm. E. SEM micrograph showing the high clay content within the matrix (Mtx) of weakly laminated foraminiferal mudstones. Illite and mixed layer illite/smectite are the dominant clays with kaolinite and chlorite common authigenic minerals. Kaolinite (K) is commonly found in filling foraminifera (Fm) chambers and replacing feldspars. Calcite (C) more commonly infills foraminifera chambers. Authigenic quartz (Q) is seen within the matrix attached to calcite grains coccolith fragments (CC). Intra particle porosity (IPP) is common within foraminifera’s and cement grains. F. SEM micrograph showing the extent of calcite cement (C) within the lime wackstones. Authigenic quartz (Q) is common in the lime wackstones and is seen attached or on top of calcite cements (C). The micrograph also shows the small quantity of matrix (illite and mixed layer illite/smectite) found between the calcite cements. G. SEM micrograph at higher magnification of a weakly laminated foraminiferal mudstone showing coccolith fragments (CC), authigenic quartz (Q), wisps of chlorite (Ch), bitumen (B), organic porosity (OMP) and clay held porosity (CHP). Coccolith fragments are the main constitute of calcite in the weakly laminated foraminiferal mudstones. H. SEM micrograph at higher magnification of a lime wackstone showing how authigenic quartz (Q) infills porosity within the calcite cements (C). Intra particle porosity (IPP) is the dominant type of porosity within the lime wackstones due to the lack of clay minerals and bitumen (B). Some clay held porosity (CHP) is still present in the lime wackstones.

Like the weakly laminated foraminiferal mudstones, free Si and Al in the pore waters aided the precipitation of kaolinite within the clay/coccolith matrix in between the isopachous cements. Electron microscopy shows the lime wackstones contain significant amounts of authigenic equant blocky quartz that sits on top and beside isopachous carbonate cements. Finer (1-3µm) authigenic quartz grains have also precipitated within pore space between coccolith grains within the matrix. We infer the Si to precipitate authigenic quartz is sourced from smectite/illite reactions and/or any remaining Si from dissolved radiolarian shells. The volume and texture of the quartz are interpreted to be late diagentic when temperatures are suitable for authigenic quartz to be precipitated. The lime wackstones contain less TOC than the weakly laminated foraminiferal mudstones and, therefore, contain less bitumen. However, some bitumen is still present between isopachous cements. Like the weakly laminated foraminiferal mudstones organic porosity is present, however this is rare due to the maturity of the sample (1.1Ro%).

Discussion

Diagenesis and paragenetic sequences

Both lithofacies identified in the Eagle Ford Fm have undergone a relatively simple paragenetic sequence (Fig 2). TOC content (6-8%) suggests anaerobic conditions during deposition of the weakly laminated foraminiferal mudstones. Organic rich sediments which have undergone anaerobic microbial metabolism contain pore waters with high concentrations of bicarbonate, iron and sulphide (Macquaker et al., 2014) The presence of non-ferroan calcite cements and frambooidal pyrite strongly suggests microbially mediated sulphate reduction caused the sequestration of iron and sulphide into pyrite and the precipitation of non-ferroan calcite cements within foraminifera chambers (Irwin, 1977, Astin and Scotchman, 1988, Scotchman, 1989). The volume and fabric of the calcite cements, together, with the preservation of uncompacted foraminifera shells indicate cements were precipitated prior to significant compaction.

The infilling of some foraminifera with kaolinite suggests kaolinite also precipitated during early diagnosis (Fig 1). The degradation of OM through sulphate reduction and the thermo-chemical decay of OM later in burial are all associated with organic acids within the pore waters (Barcelona, 1980, Crossley, 1991, Taylor and Macquaker, 2014, Macquaker et al., 2014). We suggest organic acids were dissolving silicate at an early stage of burial prior to compaction. Organic acids, such as carboxylic acid, are likely to be responsible for Al mobilisation as they dissolve Al-rich amorphous material providing the components to produce authigenic kaolinite (Macquaker et al., 2014, Fein, 1994).
Figure 2: Paragenetic sequence reconstructed for the weakly laminated foraminiferal mudstones and lime wackstones in the Eagle Ford Fm.

The precipitation of authigenic quartz is a late diagenetic process due to the high temperatures needed to precipitate quartz (Schieber et al., 2000). Due to the volume, texture and location of authigenic quartz cements in the weakly laminated foraminiferal mudstones we infer Si is sourced from either smectite to illite reactions or the transformation of biogenic silica. High temperatures related to deep burial processes see the formation of authigenic quartz and chlorite within pore space between coccolith fragments (Fig 1) and secondary pores generated through dissolution.

In the lime wackstones, thin section analysis shows foraminifera and radiolarians are fragmented suggesting an oxygenated, higher energy environment during deposition (Aplin and Macquaker, 2011) (Fig 1). The high volume of carbonate cement and the small quantity of TOC present in the lime wackstones suggest extensive OM oxidation occurred within the water column is pre deposition and at the sediment-water interface. Further analysis with CL indicate a high quantity of calcite was precipitated in one early phase. The carbonate in this lithofacies has two sources; marine waters and via microbially induced reactions; OM oxidation and sulphate reduction. All three sources precipitate cements with almost identical compositions and texture. However, carbonate cements display zonation, indicating changes in pore water chemistry (iron and manganese content) as the cements precipitate during burial (Astin and Scotchman, 1988, Scotchman, 1991, Scotchman et al., 2000). This suggests as the sediment was buried sulphate reduction became less important and iron from iron reduction was sequestered into the calcite cements, decreasing their fluorescence (Fig 1).

The calcification of radiolarians indicates that their silica content was replaced early in diagenesis. The release of Si to the pore waters allowed the precipitation of kaolinite in between isopachous carbonate grains. Blocky equant authigenic quartz sits on top and beside isopachous carbonate cements (Fig 1). The texture of the quartz cements are interpreted to be late diagenetic when temperatures and pressures are suitable for authigenic quartz to be precipitated (Schieber et al., 2000). The acidic conditions related to quartz precipitation are thought to create secondary porosity within the isopachous calcite cements(Fig 2) (Schieber et al., 2000). Some pores are left open (Fig 1), while some are infilled with authigenic quartz or kaolinite. The process is subtle within the weakly laminated mudstones.
because of the greater clay content making it difficult to distinguish secondary porosity, and quartz grains are finer (1-2µm) and spread across the whole sample within pore space instead of in equant blocks (Fig 1).

**Impacts on Porosity**

Diagenesis within the weakly laminated foraminiferal mudstones has significantly reduced porosity. The early precipitation of calcite cements within foraminifera and other biogenic material infills intra particle porosity. The micritic matrix mainly composed of coccolith fragments preserves primary porosity during burial. However pore space is infilled by authigenic silicate cements (quartz) and clay minerals (illite/smectite, kaolinite and chlorite) during late diagenesis (Aplin et al., 2006). The majority (>80%) of the porosity is micro-porosity seen within and between clay mineral grains and organic matter.

At high magnifications clay held micro-porosity and organic porosity (pores within the organic matter/bitumen) are visible in the weakly laminated foraminiferal mudstones (Fig 1). The quantity of pores and their size within the OM depends on maturity and how much hydrocarbons the OM has expelled (Driskell et al., 2012, Pommer et al., 2014). In these samples (Fig 1) pores held within the OM are typically 50-200nm with a maturity of 1.1 Ro%. Clay held pores are 90-150nm and are unlikely to produce any permeability or significant porosity (Pommer et al., 2014, Fishman et al., 2013b). Inter-crystalline porosity is present between cement grains that surround inoceramid fragments and planktonic foraminifera. Pores are typically <1µm, although it is stressed they are rare and contribute to <10% of the total porosity. Intra-particle porosity within foraminifera chambers, phosphatic grains and inoceramids fragments is present but also contributes a small portion of porosity (<5%). Pore sizes are ~1µm. Total porosity in the weakly laminated foraminiferul mudstones is ~6-7%.

The precipitation of extensive calcite cement significantly reduces porosity within the lime wackstones (Fig 1) as calcite overprints most of the matrix and biogenic content. Due to lower TOC values and clay content there is little organic or micro porosity in the lime wackstones. SEM shows the lime wackstones contain significant inter and intra-particle porosity between calcite cements and the authigenic quartz cements that overprint them (Fishman et al., 2013b). We infer that acidic pore waters associated with authigenic quartz precipitation and thermogenic organic matter complexing created the bulk of intra-particle porosity within the calcite cements. Compared to the weakly laminated foraminifera mudstones, the lime wackstones have a different distribution of pore types where a vast majority of the pores are >1µm and found within and around cements. Despite having a lower overall porosity (2-4%) compared to the weakly laminated foraminiferul mudstones, larger pore sizes are likely to contribute to more permeability (Bjorlykke et al., 2010, Fishman et al., 2013b).

**Impacts on rock properties**

Coccolith fragments present in the matrix of the weakly laminated foraminiferal mudstones preserve planar laminations and ripple marks during compaction. The precipitation of early calcite cements within bioclasts creates a stronger and more brittle mudstone allowing for the preservation of foraminifera’s and planar laminations (Macquaker et al., 2014, King and Corporation, 2010, Davies et al., 2012). The brittleness of the Eagle Ford Fm makes it an ideal source rock to hydraulically fracture, as fractures can propagate further from the well head (Arugundade and Sohrabi, 2012). Clay minerals present in the weakly laminated foraminiferul mudstones behave elastically and can infill fractures induced through hydraulic fracturing (Aplin et al., 2006, Aplin and Macquaker, 2011, Yang and Aplin, 2009, Yang and Aplin, 2004) The lime wackstones are harder, stronger and more brittle than the weakly laminated foraminiferul mudstones due to their high carbonate and low clay content allowing them to preserve >1µm intra and inter-particle porosity (Yang and Aplin, 2009, Bjorlykke et al., 2010, Fishman et al., 2013b).

Fishman et al 2013, discuss how the lime wackstones, despite their low TOC content contain more movable hydrocarbons (S1 peak in Rock Eval Pyrolysis) compared to the weakly laminated foraminiferal mudstones, which contain a higher TOC content. The weakly laminated foraminiferul mudstones mainly contain hydrocarbons stored within the bitumen, yet to be expelled (S2 peak in Rock Eval). Fishman et al. 2013, conclude the lime wackstones contain more movable hydrocarbons due to their porosity distribution, increasing permeability and be able to “store” more movable hydrocarbons compared to the weakly laminated foraminiferul mudstones. As OM matures, organic
porosity increases and more hydrocarbons are produced, however over geological timescales hydrocarbons have migrated and sit in lithologies with greater permeability.

**Conclusions**

- Both the weakly laminated foraminiferal mudstones and lime wackstones have undergone a relatively simple paragenetic regime with similar processes occurring in both.
- Anaerobic bottom waters preserved TOC within the weakly laminated mudstones, while the lime wackstones were deposited in a well oxygenated environment, oxidising organic carbon and allowed the for the extensive precipitation of calcite cement.
- The bulk of porosity within the weakly laminated foraminiferal mudstones is present as micro-pores (50-150nm) within OM and clay mineral grains. The lime wackstones contain less porosity overall, but the majority of pores are >1µm within and around cement grains creating inter-granular and intra-granular porosity.
- The lime wackstones contain more mobile hydrocarbons (S1) while hydrocarbons in the weakly laminated mudstones are stored in the bitumen (S2) and not extractable through hydraulic fracturing.

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**References**


