Reconstructing the burial diagenetic history of the fractured Lower Carboniferous carbonates of the North Wales Platform

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Word count: 56664 (with references: 66562).
Terms and abbreviations

N = North, E = East, S = South, W = West

EISB: East Irish Sea Basin
DP: Derbyshire Platform
FM: Formation
Mb: Member
Lmst: Limestone
Sst: Sandstone
Mdst: Mudstone
Ma: Million years
PDB: Pee Dee Belemnite
SMOW: Standard Mean Oceanic Water
CL: Cathodoluminescence
XRD: X-ray Diffraction
ICP-AES = Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP-MS: Inductively Coupled Plasma Mass Spectroscopy
REE: Rare Earth Elements

Fe: Iron
Mn: Manganese
Mg: Magnesium
Ca: Calcium
Sr: Strontium
Al: Aluminium
Cu: Copper
Pb: Lead
Zn: Zinc
Rb: Rubidium
Ba: Barium
Y: Yttrium
La: Lanthanum
Ce: Cerium
Pr: Praseodymium
Nd: Neodymium

Pm: Promethium
Sm: Samarium
Eu: Europium
Ga: Gadolinium
Tb: Terbium
Dy: Dysprosium
Ho: Holmium
Er: Erbium
Tm: Thulium
Yb: Ytterbium
Lu: Lutetium
HCl: Hydrochloric acid
M: Mole
Kv: Kilovolts

d = lattice spacing
OR = degree of order
k = element distribution coefficient
α = isotope fractionation coefficient

FI = fluid inclusion
°C = degree Celsius
F = degree of fill
eq. wt % = equivalent weight percentage
H = host limestones
S = bedding parallel stylolites
CV = calcite veins
D = Dolomite
C = Calcite

Geobody: a genetically related body or unit that results from a geological or diagenetic process
Reconstructing the burial diagenetic history of the fractured Lower Carboniferous carbonate of the North Wales Platform

Alanna Juerges, Degree of Doctor of Philosophy, University of Manchester, 2012

The North Wales Platform, UK represents a lower Carboniferous carbonate platform that developed during back-arc extension on the northern margin of the Wales-Brabant Massif. This succession was faulted and folded during the Late Carboniferous Variscan Orogeny and again during the Late Jurassic extension-Tertiary Alpine Orogeny, resulting in multiple reactivations of Caledonian structural trends (N-S, NE-SW and NW-SE) and basin inversion. The platform underwent deformation, several episodes of fluid-flow, and multiple phases of diagenetic overprinting. The products of fluid circulation in this area consist of the Mississippi Valley-type (MVT) mineralisation and dolomitisation, mostly affecting the carbonates of the lower Carboniferous (Dinantian) succession.

This study presents a combined regional sedimentological, diagenetic and structural framework through multiscale, interdisciplinary techniques. Techniques include field observation, transmitted light and cathodoluminescence analysis, in-situ and bulk major and trace element analysis including rare earth elements, stable isotope (oxygen/carbon), and strontium isotope analysis.

The North Wales Dinantian (Asbian-Brigantian) succession developed from a ramp to rimmed platform geometry and records a range of depositional and non depositional environments including platform margin, subtidal, peritidal and emergent. Early diagenesis comprises a series of marine and meteoric calcite cements. These are volumetrically the most important cements and occlude nearly all primary interparticle porosity on the North Wales Platform. Consequently, burial calcite cements and MVT mineralisation was precipitated within fractures and dissolution-enhanced secondary porosity. Dolomitisation on the North Wales Platform occur as pods along the current day coastline/palaeo platform margin and eight dolomite phases have been identified. These are present as matrix replacive and cement phases that are spatially and temporally related to deep seated structural lineaments.

It is proposed that early diagenesis resulted from the establishment of meteoric aquifers, influenced by tectono-eustatic fluctuations. Subsequently, small volumes of fluid were released following compaction and during the waning stages of lower Carboniferous extension. The onset of the Variscan compression during the mid – Late Carboniferous led to the main stage of basin de-watering on to the platform via faults/fracture systems and the development of pockets of overpressuring. Circulating marine pore-waters provided the necessary magnesium required for dolomitisation within select fault/fracture systems. A second phase of tectonic deformation with associated copper mineralisation occurred during the Triassic-Jurassic extension and Alpine uplift. Fluids and metals for the copper mineralisation were derived from the adjacent siliciclastic Permo-Triassic and Jurassic East Irish Sea Basin succession. Compared to the adjacent and time equivalent Derbyshire and Askrigg Platforms, the North Wales Platform displays a more complex paragenesis as a result of differing burial histories and fluid sources. This study highlights the importance of understanding palaeo-fluid flow and diagenesis in platform carbonates and is directly relevant to hydrocarbon production, mining and resource containment in reservoirs.
Declaration

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Status of papers

This thesis is presented as papers intended for publication. This section outlines the papers, current status with regards to publication and clarifies the input of co-authors.

**Paper 1:** Sedimentological and diagenetic overview
Intended for submission in the Journal of the Geological Society pending sponsor approval.

**Paper 2:** Kinematic evolution of the North Wales Platform: insights from the Great Orme
Intended for submission in the Journal of Basin Research/ Geofluids pending sponsor approval.

**Paper 3:** Dolomitisation on the North Wales Platform
Intended for submission in the Journal of Sedimentary Research pending sponsor approval.
Chapter 1: Introduction
Chapter 1

1.0 Introduction
Marine carbonate systems range in age, dating from the Phanerozoic to the modern day and occur within every environment from the poles to tropical seas (Wilson, 1975; James, 1997). They are primarily deposited on and adjacent to marine platforms that exhibit a range of forms including epeiric (Hillgärtner et al., 2003), ramps (Wright, 1992), isolated platforms (Eberli, 1991 and references therein), rimmed platforms (Burchette & Wright, 1992) although they can also occur as isolated mounds (Burchette, 1992), and precipitate within terrestrial lacustrine settings (Allen & Collinson, 1986; Wright, 1990). Carbonate systems form from abiotic and/or biotic carbonate production and are controlled by a number of environmental and depositional processes. These controls include temperature and seawater composition. These are in turn controlled by extrinsic factors such as climate, subsidence and sea-level change (Schlager, 2005). During and post deposition, marine carbonate systems are typically affected by a spectrum of diagenetic processes that modify the primary pore network. These physical and chemical processes are controlled by the composition of the host sediment, pore fluids and external forces such as pressure and temperature that change with the burial history. Diagenesis is considered to be eogenetic (near-surface), mesogenetic (burial) and telogenetic (occurring during uplift/basin inversion). The eogenetic environment includes diagenetic modification from marine and/or meteoric fluids, whilst the mesogenetic realm embraces the shallow and deep burial environments and can be influenced by a mixture of diagenetic fluids including basinal brines. Within all these environments, mineral precipitation (cementation), recrystallisation (neomorphism and dolomitisation), compaction and dissolution interact to variably occlude and enhance porosity. In addition, faulting and fracturing can occur at any point during the burial history often providing effective flow pathways for diagenetic fluids.
Chapter 1. Introduction

The diversity of composition and internal architecture within carbonate systems has been of interest for many years not only academically but within the hydrocarbon industry. The explosion in carbonate studies occurred in the 1950’ and 60’s with the discovery and exploration of carbonate hosted reservoirs (Flügel, 2004). This was followed by the rapid development of geochemical techniques and sequence stratigraphic models aimed at predicting porosity. These methodologies are now widespread in carbonate studies. A recent revitalisation in academic studies is a consequence of increased industry interest, availability of new data, development of ideas and techniques and the advent of forward modelling methodologies (Whitaker et al., 2004; Whitaker & Xiao, 2010) (see section 1.1, Applications).

1.1 Applications

Studying carbonate platforms, the relationship between diagenesis, structural history and sedimentation is of great interest academically and economically. The study of sedimentology and diagenesis of carbonate platforms and in particular platform margins can provide information about bathymetry, depositional processes and palaeo-environment. Moreover, facies analysis provides important information on initial physico-chemical conditions and palaeo-hydrological framework, which dictate later diagenetic processes. Sedimentological assessment has further relevance to slope stability studies (Schlager & Camber, 1986; Kenter, 1990). Diagenetic studies can help constrain schematic models produced from sedimentological work. Cements contain invaluable information regarding fluid migration and transport of elements. Through petrographic, isotopic and geochemical characterisation of fluid source, processes of formation and alteration can be fingerprinted.

Fifty percent of the world’s hydrocarbon reservoirs are carbonate hosted and ~60% of these carbonate reservoirs are composed of dolomite these include the Permian Basin, SW USA and the Arab Formation, Middle East (Kirkham, 2004; Saller, 2004; Braithwaite et al., 2004; Beleyneh et al., 2006). Diagenesis can affect the quality of carbonate reservoirs
through porosity destruction during cementation or porosity production through dissolution, fracturing and overprinting (Moore, 2001). Characterisation of palaeo-platforms and their hydro-geological properties creates potential for modelling palaeo-fluid flow within the fractured carbonates (e.g. Whitaker & Xiao, 2010). This is of interest not only to the petroleum industry but has relevance to other disciplines of geology such as engineering geology for predicting areas of subsidence, mine seepage and containment of resources within man-made reservoirs.

1.2 Rationale for the study

Flow behaviour in carbonate rocks is governed by the presence, size, shape and connectivity of porosity, which is generally controlled by depositional facies, mineralogy, diagenesis, and fracture orientations and distributions (Lucia, 1999; Di Naccio et al., 2005). Following deposition, sediments are subject to a variety of physical and chemical processes, known as diagenesis, leading to an often complex porosity evolution that has a primary control on a) subsequent diagenetic modification and b) recoverability of water, mineral and hydrocarbon resources that are hosted in the carbonate. In this sense, understanding the evolution and controls on porosity from deposition to the present-day is essential to mapping and predicting the distribution of flow-controlling diagenetic products.

Variations in the style of diagenesis between different platform morphologies and depositional facies highlight the control of primary sedimentary composition on the distribution of porosity and cement (Moore, 1989). However, variations in porosity distribution within a single facies often occurs and demonstrates that the composition of diagenetic fluids and their flow and reaction pathways offer major controls on porosity development (op. Cit.).

Where matrix porosity is either low or poorly connected, fractures can provide a major influence on fluid flow and can dominate the permeability architecture (Hollis & Walkden, 2002; Lonergan et al., 1999). During burial the fractures can act as important pathways for diagenetic fluids
that can either result in dissolution or cementation within the fractures and/or the adjacent matrix of the host rock. Therefore, the porosity and permeability of the matrix and fractures determines the storage and flow capacity within carbonate reservoirs (Aguiler, 1995). The presence of open fractures can result in flow rates far in excess of the matrix permeability, making understanding and characterising the diagenetic history, distribution, density and connectivity of these fracture systems imperative in determining and modelling the reservoirs flow capacity (Muir-Wood & King, 1993). However, there remains much uncertainty in how these fracture networks can be best characterised in order to best predict their spatial distribution in areas of poor data abundance and quality. In particular few studies attempt to relate regional burial diagenetic events to the structural basinal evolution, or to determine the range of influence of fluids flowing from the fractures into the matrix. In order to tackle this it is important to assess the change in mechanical and petrophysical properties and the potential for fracturing though time by combining the study of the sedimentological, diagenetic and structural history (Underwood et al., 2003; Morretini et al., 2005; Di Naccio et al., 2005).

This study focuses on the burial diagenetic history of the Lower Carboniferous (Dinantian), North Wales Platform. A detailed evaluation and characterisation of burial calcite and dolomite cements and their spatial and temporal relationships to fault/fracture networks is presented. This work builds upon and extends previous studies by Bevin & Mason (1999) and Hollis & Walkden (2002). Bevin & Mason (1999) outlined an initial paragenesis focusing on the metalliferous mineralisation within North Wales whereas Hollis & Walkden (2002) demonstrated the interplay between structural evolution, fluid flow, diagenetic reaction pathways, and mineralisation for the time equivalent Derbyshire and Askrigg Platforms. In addition, the work presented within this study provides a comparison for the time equivalent platforms but also a
contrast, as the North Wales Platform was subject to a different burial history and influenced by different basins.

The Lower Carboniferous limestone of the North Wales Platform hosts epigenetic Mississippi Valley-type (MVT) deposits and copper mineralisation these in turn are associated with hydrocarbon deposits (Parnell, 1983a, b, 1988; Neilson & Oxtoby, 2008). These deposits are thought to result from the establishment of large hydrothermal systems during structural basinal development as a result of rifting (Rakovan, 2006). By assessing the type, position and petrographic characteristics and cross-cutting relationship of the burial cements, ore deposits and associated hydrocarbons, a regional paragenesis can be better constrained. Subsequent dating analysis can help tie the genesis to known structural events.

1.3 Aims and Objectives

The aim of this project is to better constrain the burial diagenetic, fluid flow and structural history of the North Wales, Lower Carboniferous carbonate platform, and relate it to local and regional scale tectonism. More specifically, (a) Investigate the relationship between faulting, fracturing and dolomitisation within a syn- and post-rift regime; (b) Determine the importance of precursor tectonic elements and post-depositional tectonism (basin inversion) controlled patterns of fracturing, dolomitisation, calcite cementation and mineralisation; (c) Geochemically fingerprint key diagenetic phases in order to determine the origin, timing and migration pathways of diagenetic fluids; (d) Map the relationship between faults, fractures and matrix pore-occluding phases to determine the extent of fluid flux from the fractures into the matrix. This will be accomplished by fulfilling the following objectives:

1. Describe the distribution of burial diagenetic carbonate cements on the North Wales Platform.
2. Describe structural deformation across the North Wales Platform and the relationship to diagenetic features at a variety of scales.

4. Geochemically and isotopically characterise the burial cements (calcite and dolomite).

5. Determine the source, composition and migration pathways of precipitating fluids using trace element, rare earth element and strontium isotope analysis in combination with standard petrographical and stable isotope techniques.

6. Use the data generated in 1-5 to relate key burial diagenetic events to the structural evolution and burial history of the North Wales Platform.

7. Compare and contrast the nature of the burial diagenetic overprint, within the fracture and matrix pore network, with other UK Carboniferous carbonate platforms in the Variscan Orogen.

1.4 Thesis structure
This thesis is presented as primarily journal papers with complimentary chapters. Due to the nature of the thesis some repetition is unavoidable. Where papers are presented with multiple authors it should be clarified that I was responsible for the bulk of the data collection, processing and writing, the co-authors contributed through field assistance, data collection and editorial review. The outline is as follows:

Chapter 2: Tectono-stratigraphic background – includes published data for the UK and Europe but more specifically the North Wales, Derbyshire and Askrigg Platforms discussed in this study.

Chapter 3: Literature review - details previous work carried out on the North Wales platform.

Chapter 4: Methodology – an overview of the methodologies and techniques used throughout this study.
Chapter 5: Sedimentological and diagenetic overview - presents field and petrographic observation of the main lithological units and cement from across the North Wales Platform with a focus on the Great Orme. This chapter provides a palaeo-hydrological and paragenetic framework for the North Wales platform on which further geochemical analysis will be based.

Chapter 6: Kinematic evolution of the North Wales Platform: insights from the Great Orme - combines structural and diagenetic observation in order to constrain a kinematic evolution of the Great Orme. The data also provides important information on fluid flow and fluid-flow pathways.

Chapter 7: Geochemical fingerprinting of a complex dolomite body, Lower Carboniferous North Wales Platform, UK - presents multiscale field, petrographic, geochemical and isotopic analysis of the dolomite from the northern margin of the North Wales Platform. This chapter characterises the dolomite and further constrains the paragenesis. In addition, the geochemical and isotopic analyses provide important information regarding the composition and source of the fluid responsible.

Chapter 8: Synthesis and discussion - reconstructing the burial diagenetic history of the North Wales Platform draws together the data presented within the previous chapters. A schematic model of fluid migration and timing on the North Wales Platform is presented and discussed within an updated sedimentological and structural framework. Finally, the wider implications and recommendations for further work are discussed.
Chapter 2: Tectono-stratigraphic Background
Chapter 2

2.1 Tectono-stratigraphic background

The North Wales Platform is one of a number of carbonate platforms that developed during the Lower Carboniferous (Dinantian) within England and Wales. Situated on the northern margin of the Wales Brabant Massif the North Wales Platform is bounded by the East Irish Sea Basin to the north, Pennine Basin to the north-west and the Cheshire Basin to the east (Fraser & Gawthorpe, 1990). The Lower Carboniferous platforms and adjacent basins in North Wales and England have been subject to several phases of structural deformation, which have influenced not only the style of sedimentation but also the subsequent diagenesis. These deformation events range from the Caledonian compression during the Devonian (prior to the development of the carbonate platforms) to the Alpine compression in the Cenozoic (Coward et al., 2003). The regional structural trends are strongly controlled by the deep seated Caledonian lineaments and as a result the same or similar structural trends have been reactivated during each phase of deformation (Nichols, 1968; Tremlett, 1970; Readman et al., 1984; Gibbons, 1990; Lee et al., 1990; Bevin et al., 1996; Turner, 1997).

The basement structure and structural history of the UK is well constrained through geophysical and geological observation (Fraser & Gawthorpe, 1990). The UK is comprised of nine terrains as a result of amalgamated basement blocks. These have remained for the most part unaltered since the Caledonian Orogeny. However, the major fault zones bounding these terrains were reactivated multiple times throughout the Lower Palaeozoic and including the end of the Carboniferous. The Caledonian Orogeny took place between 460-420 Ma as a result of the closure of the Iapetus Ocean and the collision of Laurentia and Avalonia, and affected an area from the Moine Thrust to the Welsh Borderlands (Coward et al., 2003). It has been suggested that the UK was affected by the Acadian Orogeny around 400Ma a distinct phase of tectonism from
the Caledonian Orogeny and a precursor to the Variscan Orogeny (Coward et al., 2003). The UK was subject to several other tectonic events but with no significant lineament offsets comparatively. The greatest deformation occurred south of the Variscan front across South Wales and England (Fraser & Gawthorpe, 1990). This study focuses on the northern margin of the Avalonian Terrain which lies to the north of the Variscan front. During the Lower Carboniferous, the UK was situated close to the equator and was undergoing a period of extension in a back-arc regime, leading to the development of stable platforms surrounded by more rapidly subsiding half-grabens. The combined structural highs and tropical environment gave rise to the nucleation of carbonate build-ups that developed from ramps into rimmed platforms with continued fault movement (Somerville et al., 1989). Throughout the platform development fault and fracture systems following Caledonian trends were reactivated resulting in differential subsidence, which influenced sedimentation during the Dinantian (Gawthorpe, 1989). During the Late Carboniferous the waning stages of extension gave way to the onset of Variscan compression. The Variscan Orogeny was a result of the N-S collision between Amorica and Iberia starting between 390 and 370 Ma and affected the north-west of Europe between 370 and 290 Ma (Woodcock & Strachan, 2000). The main region of deformation occurred across south Wales, England and Europe. Caledonian trends were once again reactivated with a normal and shear sense of movement. This phase of tectonic movement has been related to widespread basin de-watering and MVT mineralisation in Ireland, UK and Belgium (Neilson et al., 1998; Wright et al., 2000; Swennen 2003).

Post-Variscan structural events are mostly characterised by extension but also include uplift and erosion followed by a series of marine transgressions. The extension prevailed throughout the Permo-Triassic and Jurassic and produced a series of rift related basins within an E-W orientated regime. Extension resulted in thinning of the crust and also produced the well studied North Sea failed rift basins to the East of the
UK and the opening of the Atlantic to the west. This phase of tectonism ceased during the Cretaceous.

The final phase of deformation affecting the UK is Alpine compression. The crustal shortening and related inversion of Cenozoic and Neogene basins occurred primarily within the south and east of the UK and southern Europe. Deformation (uplift and exhumation) has also been documented around the Irish Sea Basin. However, the cause of this movement is still debatable and has previously been suggested to have arisen in response to Palaeocene igneous activity (Turner, 1997).

2.2 North Wales Platform

The North Wales Platform is surrounded by the east Irish Sea Basin to the north, Wales-Brabant Massif to the south and the Cheshire basin to the east. The Platform represents the evolution of a ramp to land attached shelf throughout the Lower Carboniferous (Dinantian). Present day exposure covers an area of 45km$^2$ from Anglesey to Oswestry. The palaeo-platform margin is roughly situated along the present day coastline and bordering the Cheshire Basin with outcrops of natural cliff faces and disused quarries. The study area is covered by BGS Geological Sheet 108 (Davies et al., 2004) (Figure. 2.1).
Chapter 2. Tectono-stratigraphic framework

Figure 2.1 Map of North Wales displaying the extent of the Lower Carboniferous outcrops and simplified fault systems (modified from Williams & Eaton, 1993; Jerret & Sampson, 2007)

2.2.1 Stratigraphic framework
The stratigraphic framework for the North Wales Platform has remained largely unchanged since the initial publications by George et al., (1976) Hind & Stobbs (1906) and Morton (1898). Re-evaluations carried out by Neaverson (1935, 1943) Power & Somerville (1975) and George et al., (1976) accepted the designations and subsequent work further subdivided the stratigraphic units (see Banerjee, 1969; Oldershaw, 1987; and summary texts: Warren et al., 1984; Waters and Davies, 2006; Davies et al., 2004). The framework is based on paleontological data including coral, brachiopod and goniatite zonation. However, this data coverage is patchy and often poorly misused thus foraminifera zonation is more commonly adopted due to a greater abundance within the North Wales succession (Somerville et al., 1989; Davies et al., 2004).

Throughout North Wales, Lower Carboniferous sediments lie unconformably on Lower Palaeozoic basement rocks, which include arenaceous, conglomeratic siliciclastic and igneous and metamorphosed sediments. The Lower Carboniferous strata have been divided into two major units these include the Dyserth Group and the Gronant Group,
Asbian and Brigantian in age respectively (Figure 2.2). The Dinantian, Asbian and Brigantian sediments are part of the Dibunophyllum D1 and D2 zones, a system first applied to North Wales by Hind & Stobbs (1906). It has also been noted by a number of authors that the Asbian succession is the thickest within the UK (Warren et al., 1984; Al-Fadel, 1985; Williams & Eaton, 1993). The NE Wales Dyserth Group is comprised of four formations of Asbian-Brigantian age these include the Leete Limestone, Loggerheads Limestone, Cefn Mawr Limestone and Minera Formations. Lateral equivalents in NW Wales include the Pier Dolomite, Tollhouse Mudstone, Great Orme Limestone, Bishops Quarry Limestone and Summit Limestone Formations. In addition, local formation names have been adopted for various locations across the north coast of Wales partially due to the variability in platform carbonate characteristics (Figure 2.3).

**Figure 2.2.** Correlation panel for North Wales (Waters & Davies, 2006)
Correlation between NE and NW Wales is possible on a broad scale using chronostratigraphy and faunal zonation. However, due to the contrasting structural and palaeo-environmental histories lithostratigraphic correlation is not possible. These controlling factors have also produced a marked difference in sedimentation style and rate which is visible in outcrop. Outcrops to the east display relatively massive units where as metre-scale cyclicity is more prominent in the west (Warren et al., 1984). The sediments in the south of the study area around the Llangollen-Oswestry area also display cyclicity and variable thicknesses related to active faulting in the area during deposition (Leeder & Gawthorpe, 1987).

Post-Dinantian sediments are recognised only in the east of the region (Prestatyn and Holywell). These include Namurian Holywell shales and
Gwespyr Sandstones that lay disconformably above Brigantian age strata. In NW Wales there is no evidence for upper Carboniferous strata having been deposited. Furthermore, the work carried out by Williams & Eaton (1993, Figure. 5) shows an onlap of Triassic sediments onto Brigantian sediments following a considerable hiatus.

### 2.2.2 Courceyan-Holkerian

The beginning of the Carboniferous was marked by an increased marine influence resulting in the deposition of peritidal sequences comprising hypersaline gulfs and coastal plain deposits (Waters & Davies, 2006). Within stable blocks, restricted lagoons and tidal flats developed before the culmination of the transgression brought about the deposition of open marine carbonates (Davies et al., 2004). During the Courceyan-Holkerian the onset of marine transgression switched sedimentation from alluvial to marine (Walkden, 1987; Horbury et al., 1989; Vanstone, 1996). The Early Dinantian marine incursion is represented by clastic red beds (conglomeratic sandstones and red immature palaeosols) overlain by dolomitised carbonates deposited in a near shore environment (Waters & Davies, 2006). Initial sedimentation consisted of argillaceous carbonate ramp facies partially derived from the nearby Wales-Brabant Massif (Somerville et al., 1989). The sediment was deposited within a subtidal shallow marine environment that was subject to periodic sea level change resulting in hypersaline lagoon environments.

### 2.2.3 Asbian

By the Asbian, the North Wales Platform had developed from a gently dipping shallow marine ramp into a flat topped rimmed shelf (Somerville et al., 1989). The evolution of ramp to shallowing-upward, cyclic platform carbonates is punctuated by emergent surfaces. The cycles are capped by palaeokarst, palaeosols and minor volcanic deposits (Waters & Davies, 2006). Reef build-ups, such as those on The Little Orme and Prestatyn, became more prominent demonstrating faunal zonation and
fore-reef on-lapping deposits (Warren et al., 1984; Somerville et al., 1989).

### 2.2.4 Brigantian
Continued N-S extension caused thinning of the lithosphere producing faulted blocks and basins and emplacement of volcanic material (Leeder, 1982). Volcanic activity centred on Derbyshire along previous lines of weakness. Minor events also occurred around Bristol and Wenlock. However, little volcanic sediment (e.g. ash-tuff horizons) is evident across the North Wales Platform (Waters & Davies, 2006). The Alyn Valley and Vale of Clwyd faults experienced related movement during the Chadian, the Nercwys Nant-Figillt in the Brigantian and Early Namurian and the Great Ewloe during the Westphalian (Fitches & Campbell, 1987; Davies et al., 2004) (Figure 2.4). The resulting combination of subsidence and increased sedimentation is illustrated by a thickening of hanging wall sequences and growth faulting (Davies et al. 2004). The local fault movement as well as eustatic rise produced deeper-water platform carbonates (Somerville & Strank, 1984c). Towards the end of the Brigantian the sedimentation was further affected by the onset of thermal sag subsidence (Leeder, 1982; Walkden, 1987; Walkden & Walkden, 1990).

The adjacent East Irish Sea and Cheshire Basins underwent fault controlled subsidence with the deposition of basinal syn-rift shale and carbonates throughout the Early Carboniferous. During the mid-Carboniferous, the shale and carbonate deposition ceased due to the progradation of a deltaic system derived from the north (Swann & Munns, 2003).
2.2.5 Namurian

Following the back-arc extension that dominated during the Brigantian the development of block and basin topography gave way to thermal relaxation of the crust and resulting subsidence (Leeder & McMahon, 1988; Maynard & Leeder, 1992). Turbidite fronted deltaic systems initially supplied organic-rich siliciclastic sediments and mud to the deeper basins. The resulting shales were then overlain by coarse quartz-rich sheet sandstones and feldspathic sandstones indicative of a shallow marine environment (Maynard & Leeder, 1992). A combination of eustatically controlled sea level and subsidence has resulted in the deposition of marine beds and emergent surfaces with palaeosols.

2.2.6 Westphalian

Thermal sag continued into the Early Westphalian and the well established south-west and northerly prograding fluvio-deltaic systems
covered the Lower Carboniferous carbonates and infilled basin topography (Waters & Davies, 2006). The areas of deposition centred on the Pennine Basin, the Irish Sea Basin and the Variscan foreland (op. Cit.). The UK Carboniferous coast was subject to only minor marine incursions during the Early Westphalian (Guion & Fielding, 1988; Waters & Davies, 2006). The following deposition of thick delta top coal measures marks the halting of a marine influence. The ensuing tropical climate, high humidity and water logged conditions favoured the development of peat and coal (Anderton et al., 1979; Waters & Davies, 2006).

2.2.7 Post Carboniferous
Arid conditions prevailed throughout the Permo-Triassic resulting in the deposition of continental red bed facies. The change in depositional style was accompanied by subsidence during the waning stages of the Variscan Orogeny (Anderton et al., 1979; Waters & Davies, 2006). During the Early Triassic the Pennine Basin was subject to a marine transgression and then subsequently buried by up-to 5km in the Late Triassic and Cretaceous (Green, 1989). However, there is a lack of Permian and younger strata over much of the North Wales Platform at present-day. The adjacent East Irish Sea and Cheshire Basins were subject to Permian rifting (N-S), which was primarily controlled by NE-SW Late Carboniferous faults and Caledonian trends. Rifting continued until the mid-Triassic when thermal subsidence became the dominant control on sedimentation. A lack of Jurassic and older sediment in the basin indicates Tertiary basin inversion that was common throughout the UK (Swann & Munns, 2003).

2.3 Derbyshire, Askrigg and the Southern Pennine Basin
The Askrigg and Derbyshire Platforms are well documented as they represent historical examples of hydrocarbon bearing systems onshore UK. In addition, they host MVT or Pennine style mineralisation further increasing the interest with regard to diagenetic study (Fraser & Gawthorpe, 1990; Hollis, 1996, 2002). Both Platforms experienced similar
depositional and structural histories. Further details can be found in BGS survey sheet 111 (Aitkinhead et al., 1985) and 112 (Smith et al., 1979) (Figure 2.5).

Figure 2.5. Location map of the Derbyshire Platform and cross section from the platform to the adjacent basin (after Hollis, 2002)

The isolated Derbyshire Platform is located between the Edale, Widmerpool and Staffordshire Basins and bounded by the Edale Fault in the north and the Cronkston-Bonsall Fault in the south (Fraser & Gawthorpe, 1990; 2003) (Figure 2.5). The platform, established in the Lower Dinantian, evolved from a carbonate ramp into a fault-controlled rimmed shelf by the Late Dinantian (Gutteridge, 1987). The platform is characterised by cyclical, upward-shallowing lagoonal successions comprised of skeletal and crinoidal sediment with coral-algal reefs established at the margins (Hollis & Walkden, 2012). The metre-scale cycles are capped by palaeokarst, palaeosols, calcretes and volcanic ash deposits. Carbonate sedimentation in the adjacent basins included calciturbidites and debris flows (Aitkenhead et al., 1985; Gutteridge, 1991). By the Brigantian, carbonate production gave-way to siliciclastic sedimentation resulting in the development of progradational fluvo-deltaic systems. The sediment derived from the uplifted NW Highlands and the Wales-Brabant Massif during Variscan compression gradually infilled the
basins from the end of the Carboniferous (Gawthorpe et al., 1988; Gutteridge, 1991).

Similarly, the Askrigg Platform, situated to the north of the Pennine Basin, was established as a carbonate ramp during the Lower Dinantian (Tournasian-Arundian) and evolved into a fault controlled rimmed shelf (Arthurton, 1983; Gawthorpe, 1986; Gawthorpe, 1987a; Arthurton et al., 1988; Underhill et al., 1988). The platform comprises cyclical skeletal packstones and grainstones of Asbian-Brigantian age, with coral-algal boundstones developed along the platform margin (Gawthorpe, 1987a; Arthurton et al., 1988; Riley, 1991; Leeder, 1992). As with the Derbyshire Platform metre-scale, upward-shallowing successions are capped by palaeokarst, palaeosols and occasional horizons of volcanic clay (Arthurton et al., 1988). Carbonate sediments were transported into the basin via turbidites until the Late Asbian when fault related uplift and basin subsidence cut off carbonate supply. By the Late Brigantian, sedimentation had switched to siliciclastic dominated deposition with sediments sourced from the uplifted NW Highlands. During the Late Carboniferous fluvio-deltaic sedimentation became established across the Pennine Basin and gradually infilled topography (Kelling & Collinson, 1992).
Chapter 3: Literature Review
Chapter 3

3.0 Literature review

3.1 Introduction
This chapter aims to introduce the main concepts on which this research project is based. Processes and models regarding diagenesis, mineralisation, structural, and basin evolution will be briefly summarised. In order to gain a full understanding of the carbonate rock evolution, both chemically and physically over time, a multiscale, interdisciplinary approach is required.

3.2 Carbonate diagenesis
Diagenesis encompasses the processes, physical and chemical, that occur within sediment after deposition and up-to the onset of metamorphism (Moore, 2001). The study of diagenesis is generally concerned with understanding porosity evolution and palaeo-fluid flow (Tucker & Wright, 1996). Diagenesis occurs within a range of surface and subsurface environments (Figure 3.1). Marine diagenesis is characterised by micritisation, cementation and early neomorphism. Meteoric processes can greatly alter the porosity and permeability through widespread cementation, recrystallisation, dissolution and soil formation. Moreover, evaporative processes can greatly alter the geochemistry of the diagenetic fluids. With burial, increasing temperatures and pressures result in compaction, dissolution and circulation of fluids of elevated temperature. Controls on diagenesis include the temperature, occurrence of organic material, composition of the sediment, pore-fluid chemistry and fluid flow rates and the prevailing climate (Tucker & Bathurst, 1990; Tucker & Wright, 1990). Diagenesis can significantly alter the texture and composition of the host rock and complex diagenetic histories can result in overprinting and complete modification of the original carbonate rock characteristics (Moore, 1989, 2001).
Within carbonate systems the most common diagenetic products encountered include calcite and dolomite cements. By understanding the geochemical evolution of these cements and their relationship to hydrocarbons and mineralisation the timing and controls on palaeo-fluid flow can be deduced.

Figure 3.1. Diagenetic environments using a rimmed shelf example (Tucker & Wright, 1996)

3.2.1 Diagenesis on the North Wales Platform

Very little work has been carried out to date on the burial diagenetic evolution of the Lower Carboniferous limestones within North Wales. Published data is mainly restricted to Anglesey and Llangollen where patterns of marine and meteoric pore-occluding cements are comparable to those within Derbyshire and display variations in response to the Dinantian cyclicity (Gray, 1981; Walkden & Davies, 1983; Walkden & Williams, 1991). Further study documents the early diagenesis within the NE Wales Orefield (Al-Fadel, 1983).
3.2.2 Marine

Marine diagenesis can occur during deposition or redeposition; it includes micritisation, cementation and neomorphism that can be influenced by the chemistry of the seawater, presence of organic matter and/or microbial organisms (Tucker et al., 1990; Flügel, 2004).

Marine diagenesis within North Wales is represented by micritisation, early fibrous, botryoidal and syntaxial calcite cementation (Pickard, 1996). Micritisation is pervasive throughout the Carboniferous carbonate successions affecting most allochems, although, foraminifera and algal
fragments tend to be more micritised (Al-Fadel, 1983). The cements were precipitated post-micritisation (deduced from cross-cutting relationships) and are distributed unevenly across the platform with a higher abundance near the platform margin (Pickard, 1996). The early calcites form grain rimming cements with inclusion of micrite lamina and partially occlude primary interparticular porosity (op. Cit.). In addition, mottled textures have been recorded across the North Wales Platform, which have been attributed to marine, early diagenetic processes (Bathurst, 1959). Solomon (1989) documented and analysed mottled horizons within late Asbian strata. The same features were previously documented by Dixon & Vaughan (1911) who initially attributed the features to the dissolution of skeletal grains and re-precipitation of less consolidated cement. Subsequently, Bathurst (1959) described them as ‘pseudo-breccias’, invoking an aggrading neomorphism process. Orme & Brown (1963), Gray (1981) and Al-Fadel (1983) not only supported the observations and ideas of Bathurst (1959) but extended them, postulating an episode of diagenetically early patchy cementation. The mottles appear brown in contrast to the grey host limestone. This is due to the presence of irregular, sub-euhedral, inclusion-rich calcite spar. The cement within the host limestone postdates that of the mottles and comprises inclusion-free, clear, blocky calcite. The mottles appear to follow the outline of mouldic porosity and following further analysis have been found to preserve micro-organisms such as Dasycladacian algae, Koninckopora (Solomon, 1989). The diagenetic environment remains poorly constrained due to a lack of modern day analogues. However, petrographical studies indicate that the mottles formed post-marine micritisation but pre-aragonite dissolution and meteoric cementation, therefore, a marine/freshwater mixing zone environment has been suggested by Solomon (1989). Alternatively, Vanstone (1996) and later Horbury & Qing (2004) suggested the textures were related to pedogenic and groundwater calcretes. Moreover, the presence of organic material and heterogeneity of the initial rock before alteration dictated the texture and distribution of
the mottles. The mottles are directly comparable to those documented by MaCleod (1977) in Late Asbian platform carbonates in Derbyshire.

3.2.3 Meteoric

Meteoric diagenesis includes physical and chemical processes, including cementation, which occur within the sediment above and below the water Table (meteoric vadose and phreatic zones respectively) (James & Choquette, 1984). The vadose zone is associated with dissolution, bladed, columnar and pendant cement morphologies. The phreatic zone is associated with bladed, columnar, blocky and syntaxial cement morphologies indicative of more fluid saturated pore-spaces (James & Choquette, 1984; Walkden & Williams, 1991).

Evidence for the establishment of meteoric environments throughout the Lower Carboniferous succession is well documented. Evidence includes exposure surfaces, karst and the development of palaeosols (Walkden & Davies, 1983; Warren et al., 1984). Work carried out by Walkden & Davies (1983) on the limestones in Red Wharf Bay, Anglesey identified a number of emergent surfaces and related meteoric phreatic pore-occluding cements. The sandstone that plug the karst pits contain only syntaxial silica overgrowths with no carbonate cement or evidence for replacement. Comparatively, the host-limestone displays evidence of initial aragonite dissolution followed by cementation of clear, syntaxial calcite spar. The calcite has occluded all the primary porosity of which was relatively high. There is also only one generation of calcite cement where changes in the precipitation conditions have resulted in zonation. There are two distinct styles of cement that are separated by a hiatus and silica removal event. The earlier stage comprises non-luminescent calcite with thin brightly luminescent bands indicative of an oxygenated open pore system. The second is characterised by uniform, medium luminescent calcite representing a more closed system. The calcite cement has been concluded to have precipitated post aragonite dissolution due to its presence within micrite envelopes, even around
areas which would have been subject to vadose conditions, and post lithification (Walkden & Davies, 1983). In the absence of lithification cements it has been postulated that they may have occurred as micrite/microspar located at grain boundaries and produced around the same time as the aragonite dissolution (op. Cit.).

3.2.4 Shallow burial and Deep burial
The burial environment is typified by compaction (mechanical and chemical), increased temperatures, cementation or dissolution (James & Choquette, 1984).

The only study regarding shallow or deep burial diagenesis on the North Wales Platform was carried out by Bathurst (1987). The study focused on the Brigantian Cefn Mawr Limestone Formation. The quarries examined included the Pant-y-Pwll Dwr Quarry, Halkyn, Graig Quarry, Llanarmon-yn-Lal and Waenbrodlas Quarry, Halkyn, Clwyd (Figure 3.2). Throughout the quarries in Clwyd the effects of mechanical compaction and pressure-dissolution have been noted and often result in diagenetically enhanced bedding planes within more fissile limestones. The scale of the ‘beds’ ranges from 2-10cm. The fissile limestone also occurs in combination with a harder limestone that contains large allochems, which are preferentially, orientated parallel to the bedding planes (Bathurst, 1987).

The differing extent of diagenesis has been attributed to the selective cementation between the two lithologies. Bathurst (1987) concluded that the mechanical compaction must have occurred prior to pressure dissolution. Pressure dissolution seams are concentrated within the more fissile limestone and stylolites are not generally present. The evidence suggests that the sediment was relatively unconsolidated within the sediments that produced the fissile limestone.

3.3 Sources of fluid during burial
Fluids can be derived from a number of sources during burial and given favourable fluid flow pathways. These include freshwater, seawater, meteoric, formational, basinal fluids. These fluids can be transported via
a range of mechanisms such as topographic and gravity flow or by
tectonic and convectional drives. Various models have been reviewed
regarding the expulsion and migration of fluids from their source onto
carbonate platforms (e.g. Machel, 2004; Whitaker et al., 2004). However,
as it has been noted that there is no single hydrodynamic model that
adequately explains the temperature, geochemistry variations often
observed (Demming & Nunn, 1994).

3.3.1 Compaction
During the first of kilometre, sediment is subject to mechanical
compaction and dewatering whereby the grains are mechanically
rearranged, packed more closely and pore-water is expelled (Tucker &
Wright, 1990; Moore, 2001; Flügel, 2004). This results in interparticular
porosity reduction and removal of up to 70% of pore water and water
within clay mineral layers (Burst, 1969; Moore, 2001). Compaction that
occurs within platform-adjacent basins has the potential, prior to deep
burial diagenesis, to squeeze fluids onto the platform via aquifers and
permeable horizons (Garven, 1995; Warren, 2006). This mechanism has
previously been invoked for fluid expulsion related to the emplacement of
MVT deposits on the Derbyshire Platform (Berry, 1984; Walkden &
Williams, 1991). However, the mechanism does not explain the high
temperatures, usually in excess of 150 °C with salinities of up to 25wt %
NaCl, determined from fluid inclusion analysis (Sverjensky & Garven,
1992; Coveny et al., 2000; Leach et al., 2005; Neilson & Oxtoby, 2008).
The low fluid flow rates alone would not be able to retain the high
temperatures during transport and precipitation (Cathles & Smith, 1983;
Bethke, 1986).

3.3.2 Tectonic compression and topographically driven flow (hydraulic
head)
Hydraulic gradients are formed as a result of topographic variations in the
subsurface (Garven, 1995). Fluid is driven from areas of high topography
to areas of low topography. This is especially true for less than several
kilometres of burial due to the overlying water column where pore spaces remain close to hydrostatic pressures (Cox et al., 2001). The model postulates the migration of groundwater down-dip and the upward expulsion of basinal brines along palaeo-aquifers (Garven et al., 1999; Beales & Jackson, 1966). This goes some way to explaining the temperatures and flow rates and also agrees with models for the precipitation of the mineralisation (Garven & Freeze, 1984). The model, however, does not account for all MVT deposits as it does not explain some of the anomalously high fluid temperatures calculated from inclusions (Worden et al., 1999; Hollis & Walkden, 2002). In addition, there may not always be a suitable aquifer and adequate topographic contrast to produce a gradient (op cit.).

3.3.3 Gravity flow

Fluids can flow under the force of gravity where suitable permeability is available. This can include percolation either through sediment similar to seepage-reflux (see section 3.3.3) or through fault and fracture systems (Moore, 2001). Gravity flow can occur in range of environments such as passive and tectonically active margins and post-tectonic uplift (Heydari, 1997). Gravity flow is often characterised by moderate to high fluid fluxes that consist of meteoric and subsurface formational fluids. During fluid migration fluids often become mixed and modified as a result of the dissolution of metastable mineral phases within the host rock (e.g. evaporites) (Moore, 2001). The initiation of fluid flow is a consequence of contrasting topographic elevation with fluid recharge generally occurring up-dip (Heydari, 1997). The termination of gravity flow can result from a decrease in topography or within passive margins, marine transgression and closure of the recharge area (Moore, 2001). This mechanism has often been invoked for large scale fluid flow within carbonate platform environments (e.g. Garven & Freeze, 1984).

3.3.4 Convection
Convection of fluids through carbonates can occur under a variety of conditions and require a high fluid flux, suitable porosity and permeability and a density or temperature gradient (Wilson et al., 2001). Convection is generally inhibited by the presence of fine grained units and/or faults and fractures (Whitaker & Xiao, 2010). Convection can be forced or free flowing. Fluids drawn downward into carbonate successions during evaporation and replenished by seawater are termed seepage-reflux and are driven by a density contrast between seawater and pore-fluids (McKenzie, 1981). Free convection or Kohout convection occurs when seawater enters the carbonate platform under tidal currents and circulates within the platform as a result of thermal gradients (Sanford et al., 1998; Whitaker & Xiao, 2010). Thermal convection can become established within permeable sediment that overlie volcanic centres such as atolls, areas of crustal thinning due to plumes or extension or within platforms where as a geothermal gradient is able to be established between the basin and platform top (Flügel, 2004).

3.3.5 Seismic pumping
Episodic fault and fracture movement can generate coeval transient fluid migration. This process can potentially release fluids into the overlying 5 km of crust during tectonic movement (Muir-Wood & King, 1993). Fracture initiation can result from increased shear stress, dilation from granular flow and during pore-elastic processes to inelastic deformation of intergranular pore spaces (Odling et al., 1999). This establishes a fluid pressure gradient and consequential migration of fluids from the surrounding matrix into the fracture (Rutter, pers.comms.). The release in pressure or stress in the subsurface tends to cause the rapid expulsion of fluids vertically along joint systems. The change in pressure and temperature (P/T) and increased rock-fluid interaction often induces cementation (Cox et al., 2001). The cemented faults and fractures behave as effective flow barriers to subsequent fluid flows but can be reactivated during later seismic events (Sibson et al., 1975). This is true for normal faults, whereas, in a compressional regime fluids are thought
to be drawn into the faults and then expelled in the waning stages as pore-elastic rebound closes the fractures (valving) (op. Cit.). Seismic valving generally occurs where a fracture propagates from an over pressured horizon into an overlying highly permeable sequence (Sibson 2001). The result is rapid expulsion of the deep burial fluids, followed by pore fluid mixing and intense diagenesis. Repeated failure produces pulses of fluid flow and results in different phases of mineralisation (Cox et al., 2001). The volumes of fluid that can be transported by seismic pumping are in the order of $10^5$-$10^{10}$ l with a displacement of less than 1m for shallow to moderate depths (Burley et al., 1989).

### 3.3.5.1 Overpressuring

Overpressuring is not in itself a mechanism for fluid flow but can aid fluid flow when occurring in combination with compaction and/or seismic pumping. Overpressuring occurs where impermeable strata, in the absence of an aquifer, traps pore-fluids during rapid deposition (Sibson et al., 1975). The sediment is usually sealed by faults that inhibit the lateral migration of fluid and/or cemented or impermeable horizons cap, preventing vertical migration (Hunt, 1990; Powley, 1990). The pressures produced may exceed the normal hydrostatic pressure and can verge on lithostatic pressures (Sibson, 2001). During burial, the pressure gradually increases until the confining rock is breached, often expelling hot, saline, metalliferous basinal fluids (Cathles & Smith, 1983). The subsequent faulting and fracturing provide conduits for the fluid flow. Following the sudden release in pressure the joint re-seals and the build in pressure begins again. The process periodically produces fault failure and is comparable to seismic valving (Burley et al., 1989). Overpressuring can be induced or exacerbated by an increase in fluid temperature which may be related to close proximity to the emplacement of volcanics, the increase in salinity due to filtration by osmosis, generation of hydrocarbons and production of methane or the release of interlayer water from clays (Bradley, 1975).
3.3.5 Lower Carboniferous

There have been no fluid expulsion models proposed for the North Wales Platform to date. However, it has been postulated that pre-Carboniferous and potentially early carboniferous fluid flow around the Llanfair and Llanrwst areas fields resulted from a mixture of basinal derived brines expelled via faults and downward migration of meteoric fluids (Haggerty & Bottrell, 1997). The adjacent Derbyshire and Askrigg Platforms have been studied much more extensively and a number of models proposed. These include compaction driven flow during early diagenesis followed by overpressuring and tectonically driven fluids during late diagenesis (Hollis & Walkden, 1996, 2002) (see chapters 7 and 8 for further discussion).

3.4 Dolomitisation

Dolomitisation is a process whereby calcium carbonate is replaced by dolomite (magnesium carbonate) or precipitates directly as dolomite cement. The process can lead to reduction in rock volume by up-to 12% and can also increase interparticular porosity (Braithwaite et al., 2004; Flügel, 2004). In addition, dolomitisation can profoundly modify rock properties by increasing the rigidity and brittle nature compared to a precursor limestone. This can enable the preservation of porosity to great depths (>5km) (Choquette & Pray, 1970), decrease the likelihood of stylolitisation and favour fracturing (Bouch et al., 2004). Conversely, continued dolomitisation can obliterate primary rock textures such as sedimentary structures and even remove porosity and permeability through complete cementation and overprinting. This is often referred to as overdolomitisation and can also be accompanied by the precipitation of late diagenetic calcite and/or anhydrite, which would also act to reduce porosity (e.g. Jones & Xiao, 2005). This has led to increasing interest by the hydrocarbon industry as dolomitised limestone can act as an effective reservoir or completely remove favourable reservoir properties. Of particular interest is the characterisation and prediction of dolomite bodies and associated porosity and permeability (Machel, 2004). Comparatively, academic interest has focused on characterisation and process of
formation. Dolomitisation remains an enigmatic area of study due to the difficulty of dolomite formation related to kinetic factors with the exception of experiments that duplicate microbially mediated, low temperature, anaerobic, saline conditions such as those observed in the Coorong lakes of South Australia (Braithwaite et al., 2004; Wright & Wacey, 2004). Nevertheless dolomites have been recorded, unevenly, throughout geological history and from a range of environments (op. Cit.) (Figure 3.3).

In addition, the study of dolomites in general has been hindered by the lack of modern day analogues, all of which is often referred to as the ‘dolomite problem’ (Machel & Mountjoy, 1986; Warren, 2000; Flügel, 2004). The key controls on dolomitisation include Mg availability, temperature, fluid flux rates, CO$_2$ availability and the composition of precursor carbonate (Machel, 2004).

Dolomitisation can form under a variety of conditions and therefore a number of models have been proposed. These include evaporite associated mechanisms such as seepage reflux and drawdown, models (e.g. Grosmont, Canada Jones et al., 2003), compaction and convection (e.g. Ireland Wright et al., 2004). These models are outlined below.

3.4.1 Evaporitic hypersaline, reflux and sabka dolomite

Dolomite is formed from water where the salinity is controlled by evaporation in a near surface and shallow burial environment (Machel, 2004). The dolomites are penecontemporaneous and post-depositional and precipitated during the early diagenetic history (op. Cit.).

Reflux: evaporation and limited circulation of fluid within a lagoon behind a barrier increases in density during evaporation and as a result flows downwards into the sediment and dolomitisation occurs within the near surface. The resulting dolomitisation is often pervasive, up to platform and basin scale (Potma et al., 2001) and can form stratiform deposits (e.g. Permian Basin, West Texas and New Mexico, Adams & Rhodes, 1960). A second type of reflux known as latent reflux has also been identified by Jones et al., (2002), which is driven by greater density of brines and as it migrates downwards it entrains seawater and disperses laterally. The
resulting dolomitisation occurs in smaller volumes compared with the reflux model (Machel, 2004).

Sabka: sabka dolomitisation is related to reflux dolomites although they produce lower volumes of dolomitisation (Machel, 2004). Sabkas are deflation surfaces in supratidal environments that are periodically inundated by marine water. Similarly to reflux models, following inundation evaporation increase the salinity and density of the marine waters that migrate downwards into the sediment (Morrow, 1982). As a result the dolomite associated with periodic flooding generally occurs at the top of shallowing upward sedimentary cycles, within the few metres and where pore-waters become locally reducing, more alkaline and sulphate reduction takes place (McKenzie, 1980; Morrow, 1982; Machel, 2004). In addition, a major by-product of sabka dolomitisation includes the precipitation of sulphates, which form a range of textures e.g. chicken wire anhydrite (Butler, 1969; Bosellini & Hardie, 1973).

Some of the most prolific ancient examples of evaporative and early diagenetic dolomites occur within the Middle East, Permo-Triassic and Cretaceous successions (e.g. Khuff and Arab Formations, Ehrenberg et al., 2007; Esrafili-Dizaji & Rahimpour-Bonab, 2008, 2009) and modern day equivalents (e.g. Abu Dhabi Butler, 1970; McKenzie, 1980; Muller et al., 1990).

3.4.2 Bacterially mediated dolomite

A number of contrasting views have been published with regard to the role of sulphate in the formation or inhibition of dolomitisation (Wright & Wacey, 2004). Previous studies have demonstrated that the presence of sulphate can inhibit calcite precipitation and, due the kinetic barriers and the formation of neutral ion pairs with Ca and Mg, would therefore inhibit dolomite precipitation too (Walter, 1986; Wright & Wacey, 2004).

However, Brady et al. (1996) argued that sulphates could be a catalyst for dolomitisation due to the close spatial relationship of dolomite to sulphates in modern and ancient environments (e.g. evaporites). Subsequently, it has been noted that type locations such as the Coorong
lakes don’t have any solid sulphate sediments but do host abundant sulphate reducing bacteria (SRB) communities (Wright & Wacey, 2004). Bacterially mediated dolomite can range in carbon isotope values and in the case of the distal Coorong lakes they generally fall within ‘normal marine’ values (Op. Cit.).

3.4.3 Meteoric-marine mixing dolomite
A coastal mixing zone model was first proposed by Hanshaw et al., (1971). The model suggests that dolomitisation occurs within a hyposaline environment as a result of the presence of brackish water within a freshwater-seawater mixing zone (Machel, 2004). Moreover, precipitation can occur in unconfined or deeply confined aquifers in the landward part of the platform. This relatively early process is thought to take place pre-compaction (Tucker & Wright, 1996; Flügel, 2004). The model has been invoked by several authors for thick or pervasive dolomite occurrences especially at platform margins (e.g. Land, 1973; Choquette & Steinen, 1980). However, it has later been argued that although these dolomite occurrences do exist, the mixing zone model the interpretations were based on some incorrect assumptions (Machel & Mountjoy, 1990; Machel, 2004). Moreover, the extent of dolomitisation suggested to be capable from a mixing zone model has yet to be proven in a modern or ancient example and also may even be impossible (Machel & Mountjoy, 1990; Melim et al., 2004). Due to the salinity ranges and supersaturation with respect to calcite, aragonite and dolomite, dolomitisation is not favoured. Where the mixing zone is undersaturated with respect to calcite, calcite dissolution rates are much greater than dolomite nucleation (Smart & Whitaker, 2003). Thus cave formation is more likely than dolomitisation (Whitaker et al., 2004). Where dolomite does occur in a mixing zone it tends to be in very minor volumes as fringing cements or minor replacements (Machel, 2004).
3.4.4 Seawater dolomite

Seawater with a high concentration of Mg\(^{2+}\) pumped through the carbonate platform sediment can potentially overcome kinetic barriers (such as temperature and salinity) and result in dolomitisation (Land, 1985). The driving mechanism for the pumping is mainly considered to be tides and currents but downward reflux of saline waters or thermally driven convective flow in close proximity to volcanic activity have also been considered (Carballo et al., 1987; Flügel, 2004). Examples of seawater or modified seawater dolomites include Devonian Alberta (Mountjoy et al., 1999), Carboniferous Ireland (Gregg et al., 2001), and the Cenozoic Bahamas (in this case the processes remain debatable - Whitaker et al., 1994; Sanford et al., 1998; Machel, 2004).

3.4.5 Burial dolomite

Compaction and expulsion of basin derived fluids with a significant concentration of Mg\(^{2+}\) can result in dolomitisation (Machel, 2004). The release of the Mg\(^{2+}\) is thought to occur during the transformation of clays (smectite to illite) with increasing burial depth and with elevated temperatures (Flügel, 2004). Other sources of fluids considered are hydrothermal when the temperature of dolomitising fluids exceeds that of the host-rock limestone, metamorphic and localised fluids during stylolitisation (pressure solution) (Morrow, 1982).

Burial dolomites are recognised by the presence of coarse crystals that often have curved faces or undulose extinction (e.g. saddle dolomite), which suggest formation at temperatures in excess of 60-80°C (Radke & Mathis, 1980; Gregg & Sibley, 1984). Burial dolomites can have appreciable iron content within the crystals, occur syngenetically with stylolites and, in most cases, replaces the host-rock matrix. The saddle dolomite or baroque dolomite is characterised by curved crystal faces due to twisting of the c-axis (Tucker & Wright, 1990; Moore, 2001; Flügel, 2004). The curved crystals faces can also be achieved by thermo-chemical sulphate reduction (TSR) or from ‘hydrothermal’ fluids of elevated temperatures regardless of the source (Machel & Lonnee, 2002;
Flügel, 2004). During burial dolomitising fluids can be expelled by a number of mechanisms such as compaction, topographic head, fault movement, and convection (Figure 3.3). These fluid drives have been invoked for many dolomite occurrences. However, the importance of fault and fracture networks acting as permeability pathways for dolomitising fluids is being increasingly recognised within diagenetic studies (e.g. Gale et al., 2004). Within the UK, burial and fracture related dolomite has been postulated as a model for the Derbyshire Platform (Hollis & Walkden, 2012).

Figure 3.3. Schematic diagram displaying different dolomitisation models (Tucker & Wright 1996; Flügel, 2004)

3.4.6 Dolomitisation on the North Wales Platform

Dolomitisation is present as pockets along the North Wales palaeo-platform margin with the most pervasive occurrence observed on The Great Orme (Warren et al., 1984). The dolomite encountered is locally concentrated along faults and fractures, contains numerous vugs and is often referred to locally as ladder dolomite (Oldham, 1987; Lewis, 1996).
Large saddle dolomite crystals line the fractures and vugs, are often observed in combination with bitumen and diagenetically late and potentially related chalcopyrite (Iker & Stanley, 1996). Porosity principally comprises interconnected vugs, intercrystalline pore space and fracturing (15% up-to 40% in areas of leaching) (Oldham, 1987). The dolomites are laterally surrounded by and have a clean sharp contact with unaltered, non-porous Asbian platform-limestone (Great Orme Limestone Fm) and these are overlain by tight Brigantian – Early Namurian limestones with interbedded shales (Figure 3.4, Warren et al., 1984). The 100m thick succession comprises vuggy and non-vuggy horizons of heavily dolomitised Asbian platform limestone (Lewis, 1996).

The exact timing of dolomitisation is debatable but is suggested to have occurred late in the cement history from fluids of elevated temperature which were possibly hydrothermal (Oldham, 1987). The control on the vertical extent of dolomitisation remains unresolved, either resulting from the overlying palaeokarstic surface or sealed by a subsequent marine shale interval (Warren et al. 1984). Determining the controlling factor would have a large bearing on the timing of the dolomitising event. Dinantian strata generally cemented early in its history therefore, if the palaeokarst surface was the dominant controlling factor then dolomitisation could have occurred early, whereas, if it was the shale interval dolomitisation could be much later (Oldham, 1987; Grayson & Oldham, 1987).

This study demonstrates the dolomites within North Wales are a result of varied precipitation mechanisms evident from textural and geochemical analysis that in many cases contradict the proposed model of Oldham (1987). Therefore, re-evaluation of the dolomites forms a key component of this PhD thesis (see chapters 5, 6, 7).
Chapter 3. Literature review

Figure 3.4. Map of North Wales and the Lower Carboniferous outcrops and a schematic stratigraphy for the Lower Carboniferous; HY- Halkyn, TR- Trefor Rocks, MN- Minera (after Warren et al., 1984)

3.5 Hydrocarbons

Hydrocarbon inclusions within calcite cement phases are abundant throughout the Carboniferous limestones of the North Wales Platform and display a close relationship with the Pb-Zn (Cu) MVT mineralisation. The predominantly uraniumiferous deposits have been recorded on The Great Orme, Halkyn (Bevin & Mason, 1999), Llandulas, Llanarmon and as far south as Minera (Parnell, 1988; Eakin & Gize, 1992; Bevins, 1994). In addition, bitumen inclusions have been observed within minor fluorite mineralisation in the Halkyn area (Parnell & Swainbank, 1990).

3.5.1 Composition and distribution

Solid bitumen inclusions are located within fluorite hosted by the Asbian and Brigantian limestone. From previous studies carried out by Greg & Lettsom (1958), Smith (1973) & Parnell (1983) the deposits are highly uraniumiferous (2.5%) and generally contain relatively high quantities of organic sulphur (6%) (Parnell, 1983).
Samples analysed from The Great Orme Mines support the results for uranium and sulphur, however, no thorium (Th) is present and only 0.1% constitutes zinc and the hydrogen/carbon atomic ratio (H/C) are consistent with anthracite values (op cit.). Eakin & Gize (1992) have suggested that the lack of Th, below the limits of accurate detection, is a result of low temperature formation.

The Great Orme mines, Northeast Wales Orefield have yielded hydrocarbon samples that do not contain sulphides but do comprise high concentrations of Cu (>1000 ppm) in close proximity to copper mineralisation (Parnell, 1983). The isotopic composition displays primarily heavy hydrocarbons (c. -25.0 per mill, carbon) and it has been postulated that the source maybe localised claystones within the Carboniferous limestone (Armstrong et al., 1997).

Deposits studied in Pant Quarry, Halkyn occur as solid masses with a concoidal fracture within calcite whereas deposits to the south in Cefn Mawr Quarry are associated with purple fluorite located in slickenside mineralised striations (Bevins & Mason, 1999).

Deposits located at Ty Gwyn and Llandulas form botryoidal masses that contain uraniferous mineralisation inclusions (pitchblende) of between 5 and 20μm (Eakin & Gize, 1992). Within the NE Wales Orefield this tends to be a large number of ordered spherical or wedge shaped inclusions. Initial study by Parnell (1988b) postulated a mechanism for ordered precipitation by exsolution following an early phase of uranium enrichment. The limited mineralisation in the hydrocarbon itself is probably a direct result of the organic matter acting as a redox (Eh) buffer (Eakin & Gize, 1992). Many of the samples display microscopic fracturing and related inclusion trails as a result of post formation radiation and movement (op. Cit.).

Potential source rocks include the Brigantian basinal shales, the Namurian Holywell Shales, Westphalian oil shales and Cannel Coals and bituminous coals. The latter, outcrop on the margins of the Cheshire Basin to the east of the platform and are predominantly gas prone (Swann & Munns, 2003). However, The Holywell Shales are the most
likely source for the hydrocarbon inclusions throughout the Northeast Wales Orefield. This conclusion has been reached due to their stratigraphical position (Figure 3.5) and when compared with the isotopic values, hydrocarbon products and source shales for the crude oil from the Liverpool Bay field there is a good correlation (Armstrong et al., 1997). The bitumen deposits in Holywell demonstrate an in situ generation of waxy solid hydrocarbons that consist of heavy nC25+ species (op. Cit.). Biomarkers have been analysed to determine the maturity of the source rocks at the time of expulsion yielding a range of 0.75-0.85% Ro or corrected values of 0.6-0.7% Ro using vitrinite reflectance analysis. This defines the window for the first phase of hydrocarbon generation in the Liverpool Bay area (Armstrong et al., 1997).

Figure 3.5. Schematic diagram of the North Wales Platform margin and isotopic signature (Armstrong et al., 1997)

3.5.2 Timing and migration
From research carried out by Parnell (1988a, b), Eakin & Gize (1992), Armstrong et al. (1997) and Bevins & Mason (1999) the migration of hydrocarbons at the margin of the North Wales Platform is suggested to have occurred contemporaneously to the flow of hydrothermal fluids. The close temporal and spatial relationship with sulphide mineralisation would
also have also provided an active reductant during the precipitation of the uranium mineralisation. The calculated age using lead isotope ratios ($^{207}$Pb/$^{206}$Pb) for samples from Ty Gwyn, The Great Orme, produce an age of migration/interaction with uranium of 256 ± 23 Ma (Parnell, 1994). This is assuming that precipitation occurred relatively quickly after or during migration and that migration of daughter lead isotopes does not extensively affect the overall ratios. This derived age places hydrocarbon migration during the Late Permian. During the Late Permian the Dinantian succession of the North Wales Platform would have resided at shallow depths following exhumation during the Variscan Orogeny (Al-Fadel, 1983; Floodpage, 2001). In addition, the Late Permian date is at odds with the regional and basinal burial history, which suggests minor hydrocarbon generation occurred during the late Carboniferous within the East Irish Sea Basin prior to Variscan compression and main stage generation occurred during the Jurassic (Hardman et al., 1993; Floodpage, 2001). This suggests that the dates obtained may not be accurate or that the hydrocarbon may have been locally emplaced as suggested by Armstrong (1997).

3.6 Mineralization

The mineralisation considered within the project is the Pennine Style and Mississippi Valley-type (MVT) deposits within the UK and in particular North Wales. The Pb-Zn (Cu) deposits of, in some cases, ore grade have been mined for thousands of years (Ford & Quirk, 1995; Bevins & Mason, 1999). The occurrence and distribution of the deposits are intrinsically linked to the development of the basin and often form kilometre-scale districts (Ixer & Vaughan, 1993; Rakovan, 2006).

3.6.1 MVT and Pennine deposits

The Mississippian Valley-type deposits are found world-wide and the largest and most well known include the Mississippi Valley Drainage Basin; Pine Point Canada; The Viburnum Trend, Tri-state District
The hydrothermal ore deposits possess similarities such as: (1) simple mineralogies dominantly Pb-Zn and in some cases Cu, (2) low formation temperatures typically 100-150°C, (3) epigenetic emplacement with a strong lithological and structural control on distribution, (4) sourced from highly saline basinal brines, (5) they produce barite and fluorite gangue mineralisation (Rakovan, 2006). Deposits display a diverse range of characteristics from precipitation style, trace element source, dominant and gangue mineral phases to emplacement style and it is this diversity that is considered to be a key characteristic of MVT deposits (Rakovan, 2006). However, the lack of a refined definition has led to the development of sub-classes. For example the Illinois-Kentucky Fluorspar and the Pennine Style mineralisation (UK) differ quite a lot from the other sub-types due to the anomalously high concentrations of fluorine (Dunham, 1974; Ford & Quirk, 1995; Fisher, 2004; Rakovan, 2006). The result of this high concentration is the precipitation of fluorite or fluorspar as the dominant gangue mineral. The source of the fluorine still remains a subject of debate and has often been attributed to the close proximity of volcanics (Plumlee et al., 1995; Rakovan, 2006).
Figure 3.6. Distribution of Mississippi Valley-type deposits and districts worldwide (from Sangster, 1990 and Paradis et al., 2007). BHT = Broken Hill-type, MVT = Mississippi Valley-type, SEDEX = sedimentary exhalative, and VHMS = volcanic-hosted massive sulphides.

3.6.2 Copper mineralisation
Copper mineralisation has been identified throughout Ireland, central England and on the north coast of Wales (Holmes et al., 1983). The mineral deposits are mainly hosted by Permo-Triassic basin fill comprised of fluvio-deltaic mud and sandstones. However, mineralisation is also observed within Carboniferous platform carbonates and hosted by basin margin faults. These deposits are thought to have been emplaced during fluid migration through the Permo-Triassic sediment and along faults (op. Cit.). Within North Wales it has been suggested that the copper mineralisation comprises part of a copper-dolomite association (Ixer & Stanley, 1996). Such associations are evident within Ireland where the copper-dolomite mineralisation occurs marginal to MVT mineralisation, is closely related to evaporites and hydrocarbon and thought to form as a result of late stage basin dewatering (Andrew, 1993; Ixer & Stanley, 1996). However, within North Wales there is no evidence for the
presence of evaporites and only minor hydrocarbon would have been expelled during the Variscan compression (Al-Fadel, 1983; Floodpage, 2001) (see chapter 6 and 7). Moreover, this study contains field and petrographic observation that suggest the copper mineralisation post-dates the dolomitisation (see chapters 5, 6 and 7).

3.6.3 Mineralisation on the North Wales Platform
The mineralisation hosted by the North Wales Platform has been exploited for many years and includes mineral ores such as copper, lead and zinc. The mining industry dates back to the Bronze Age (Lewis, 1996; Ellis, 1998; Ixer & Budd, 1998). However, at present day quarrying is mainly concerned with the limestone and that is used in the aggregate and cements industries. Metalliferous mineralisation occurs along fault planes, solution cavities and metasomatic veins (Walkden, 1987; Ixer & Vaughan, 1993). The faults are predominantly tensional dip faults that strike N-S, E-W and/or NW-SE (Davies et al., 2004). Mineralisation assemblages on the North Wales Platform, including the NE Wales Orefield, comprise stratabound or fracture controlled disseminated sulphides, which maintain a simple mineralogy and include galena (silver), sphalerite, baryte, minor fluorite, quartz, chalcopyrite, cerussite, and smithsonite. Gangue minerals include calcite, dolomite and minor volumes of quartz (Bevins & Mason, 1999; Mason & Malpas, 2006). Common assemblages include:

1. Pb-Zn-Ba-F. The predominantly lead-zinc mineralisation is concentrated in the North East Wales Orefield is hosted by the Loggerheads and Cefn Mawr Limestone and terminates against the Basement Beds underlying the Carboniferous succession and against the overlying Cefn-y-Fedw Sandstone or the Holywell Shales (Earp, 1958). Barium (baryte) mineralisation occurs in small volumes in association with lead-zinc mineralisation around Ruthin and Rhuallt (Earp, 1958; Warren et al., 1984 whereas larger volumes are hosted by bed parallel veins on the Little Orme (Warren et al., 1984) (see
Figure 3.2). Fluorite only occurs in minor volumes within the east of
the district (op. Cit.).

2. Cu. Llandudno and The Great Orme are situated to the north west of
the Northeast Wales Orefield and comprise carbonate hosted copper
deposits (Figure 3.2). Parnell (1983) postulated that the Cu derived
from saline basinal brines was present as organic complexes. This is
supported by the lack of sulphides within hydrocarbon deposits and
the high concentration of Cu and copper mineralisation. Therefore, it
has then been suggested that the metal migration was not only
contemporaneous with that of hydrocarbons but the Cu was
transported in an oil emulsion (op cit.). Small volumes of copper have
been recovered from veins in the Clwydian Range (Collins, 1975).
However, larger volumes have been observed and recovered from the
Great Orme, NW platform margin (Lewis, 1994, 1996; Ixer & Stanley,
1996). The Great Orme is host to copper/iron ore and minor amounts
of Mississippi Valley-type (MVT) mineralisation (Ixer & Stanley, 1996;
Ixer & Budd, 1998).

3. Ni-Co-Mn. Minor volumes of Nickel-cobalt-manganese have been
recorded from the north-eastern margin of the platform, Dyserth
(Strahan, 1890; Bevin & Mason, 1999)

4. Fe. Iron mineralisation presents as hematite and rarely limonite. The
ores have been worked from veins and N-S trending faults within the
Foel and Llanarmon Limestone Formations (Strahan, 1890; Davies et
al., 2004).

3.6.4 Lithological control
The distribution of the metalliferous mineralisation has partially been
controlled by the lithological architecture of the Dinantian succession.
Where mineralising fluids have penetrated the interparticular matrix
porosity adjacent to faults, mineralisation has been observed to be
concentrated below impermeable horizons of shale (Ixer & Vaughan,
1993). The shale horizons occur in the hanging wall of many of the
mineralised faults. In addition, replacive flats have been observed
immediately below chert horizons within the Brigantian Gronant Group and below the Namurian Cefn-y-Fedw Sandstone (op. Cit.). This would suggest that the shale and chert provided impermeable barriers under which the hydrothermal fluids ponded. Mineralisation in the south of the NE Wales Orefield is evenly distributed throughout the Dinantian limestone and thin intercalated shale horizons pose less of a fluid flow barrier (Ineson, 1976; Ixer & Vaughan, 1993).

3.6.5 Structural control
The orientation of structures is a dominant control on the type and volume of mineralisation across the North Wales Platform. The majority of the MVT deposits are located within E-W and NW-SE trending faults and related fractures. The N-S orientated faults and joints display mainly calcite cementation with rare sulphide deposits (Bevins & Mason, 1999). In contrast to the majority of the North Wales Platform, Minera presents Pb-Zn mineralisation, galena and sphalerite respectively along N-S and NW-SE trending faults and dominant gangue quartz cement. Minera is located to the south of the NE Wales Orefield and is situated below the E-W striking Llanelidan Fault which is offset from the rest of the NE Wales Orefield by 6km to the east (Ixer & Vaughan, 1993). The quartz gangue may be related to the joints that extend into the overlying Cefn-y-fedw Sandstone (Mason & Malpas, 2006). It has also been noted that throughout North Wales not all faults are mineralised such as the Alyn Valley Fault (Davies et al., 2004) (Figure 3.2). This may suggest that not all faults were active during fluid flow and mineralisation events. See chapter 6 for further discussion.

3.6.6 Zonation
Much of the sulphide mineralisation is situated to the north and east of the North Wales Platform (Bevin & Mason, 1999). Smith (1973) recorded a decrease in zinc/lead ratios away from Silurian rocks of the Clwydian Range and suggested that it may constitute a broad regional zonation for sulphide mineralisation. However, no convincing regional zonation for the
metalliferous mineralisation has been identified within North Wales. This is similar to the Derbyshire Platform where initial fluorite and baryte zones were defined by Dunham (1952) and Ford & Ineson (1971). It was suggested that hot basinal brine migrating from the east deposited fluorite first and as the fluids cooled baryte was deposited. However, this was later disputed by Atkinson (1983) and Ixer & Vaughan (1993) following continued quarrying of metalliferous minerals and discovery of fluorite westwards of the eastern platform margin. In contrast, zonation was identified on the Askrigg Platform (Small, 1978).

3.6.7 Paragenesis

Little work has been carried out regarding a regional paragenesis for the North Wales Platform. Smith (1921) first recognised a complex sequence, which has subsequently been updated by Bevin & Mason (1999). However, in both cases the dominant quartz gangue mineral in the south of the platform has been overlooked as it is unique to the Minera region. The paragenesis is also largely unsupported by fieldwork. A generalised paragenesis after Bevins & Mason (1999) is shown in Figure 3.7.

Figure 3.7. Generalised paragenesis for the Lower Carboniferous, North Wales, UK (Bevins & Mason, 1999)
3.6.8 Fluid composition, temperature and timing

Little to no data is available regarding the analysis of fluid inclusions and therefore the evolution and source of the precipitating fluids is poorly constrained. Work that has been carried out by Smith (1973) and Ixer & Vaughan (1993) yielded salinities of 24 wt. % NaCl equiv from fluid inclusion hosted by fluorite mineralisation. This value is considered to be comparable to basin derived oilfield brines (Ixer & Vaughan, 1993). Further analysis of fluorite fluid inclusions yielded a temperature range of 105-130 °C (Smith, 1973). In combination with the salinity data the temperature range supports the current theory that the precipitating fluids originated as deeply buried, saline brines from the surrounding basins (Ixer & Vaughan, 1993). Migration of the precipitating fluid is thought to be predominantly along NW-SE orientated faults based on field observations (Ixer & Vaughan, 1993).

The timing, source and mechanism of the fluid expulsion and mineralisation is very poorly constrained. Early studies by Earp (1958) have postulated a post Permo-Triassic age based on field evidence. Whereas, Moorbath (1962) provided a single model age of 170 ± 80 Ma (Jurassic) based on lead isotope analysis. However, later authors have suggested this is probably incorrect due to the poor quality of the sample material used (Ixer & Vaughan, 1993). Earp (1958) initially proposed that the presence of a deeply buried igneous rock was the source and drive of circulating magmatically derived fluids. However, this theory was discounted due to the general lack of field and geophysical evidence (Bott, 1968). Lead isotope dates of 240Ma (early Triassic) (Fletcher et al., 1993) and 248Ma (Parnell & Swainbank, 1990) were obtained for contemporaneous deposition of uraniferous hydrocarbon and metalliferous mineralisation from the Clwyd Mining District.

Subsequent work by Dunham (1966), Smith (1973), Ineson (1976) Ixer & Vaughan (1993) and Bevins (1994) suggested, using the limited field and isotopic data, that the most likely source of the mineralising fluid would be the adjacent East Irish Sea and Cheshire Carboniferous and Permo-Triassic Basins. The mechanism for expulsion and transport, tectonic
compression during the Variscan Orogen, has only been briefly proposed by Oldham (1987). Suggested fluid sources stem from the models produced for the Derbyshire Platform however, limited data regarding the trace elements responsible for the mineralisation on the North Wales Platform leave the sources remain poorly constrained. The mineralisation within Northeast Wales is thought to have formed at the end of the Carboniferous through to the Mesozoic from a combination of extensional tectonic and reactivation of earlier structures resulting in the expulsion of hydrothermal fluids (Mason & Malpas, 2006). The expelled fluids migrated into the older uplifted Carboniferous rocks concentrating ore mineralisation along palaeokarstic surfaces, faults and associated fractures. Comparative mineralisation took place in the Llanfair and Llanrwst deposits, NW Wales (Haggerty & Bottrell, 1997). Late stage mineralisation included Pb-Zn (Cu) with calcite and dolomite gangue cementation. The mineralisation is thought to have formed during the waning stages of an older hydrothermal system (op. Cit.). Extension in the Lower Carboniferous followed by the onset of Variscan compression reactivated faults and fracture systems, reducing the temperature and pressure and introducing surface derived fluids; this led to emplacement of aforementioned mineralisation (Haggerty & Bottrell, 1997).

The fluid source for the hematite mineralisation is not known and is suggested to be a result of circulation and leaching from the underlying basement beds or overlying Permo-Triassic sediments (Davies et al., 2004)

3.7 Trace elements

Trace elements for mineralisation and cementation can be derived from host-rock limestones (basinal and platform), clays onto which the elements can be adsorbed, organic matter and detrital minerals (sulphides) (Beales & Jackson, 1966). However, shales provide the most potential due to high concentrations that are readily released during
compaction (op. Cit.). Release of trace elements usually occurs during diagenesis through the breakdown of detrital minerals and conversion of High Mg calcite and anhydrite to low Mg calcite (Dunham, 1983).

The movement or cycling of trace elements such as carbon, iron, sulphur and manganese involve redox reactions (Snoeyink & Jenkins, 1980). The redox potentials of trace elements are not absolute and comprise two parts; the oxidation potential and the reduction potential. The overall potential of a reaction can be summarised into two equations depending on whether the state at which the reaction occurs is standard (25 degrees Celsius (°C), 1 atmospheric pressure, and one unit activity for all species) (Eq. 1-0), or non standard (Eq. 1-1) (Snoeyink & Jenkins, 1980).

\[
E^\circ = E^\circ_{\text{ox}} + E^\circ_{\text{red}} \quad \text{Eq. 1-0}
\]

\[
E^\circ_{\text{ox}} \text{ and } E^\circ_{\text{red}} \text{ are oxidation half reaction and reduction half reaction, respectively.}
\]

\[
E = E^\circ - \frac{RT}{nF} \ln Q \quad \text{Eq. 1-1}
\]

Where;
R = gas constant
T = absolute temperature, °K
n = number of electrons involved in the reaction
F = the Faraday number
Q = the reaction quotient

Redox reactions only occur at given redox levels which are controlled by solute concentrations (e.g. via dissolution/ precipitation of minerals), alkalinity of the parent fluid, and presence of organic matter (Algeo & Maynard, 2004). Trace elements commonly exhibit considerable enrichment in organic- rich facies, especially those deposited under euxinic conditions and, conversely, little if any enrichment in well

“This pattern exists because (1) many trace elements have multiple valence states, and the reduced forms that exist under low-oxygen conditions are more readily complexed with organic acids, taken into solid solution by authigenic sulfides, or precipitated as insoluble oxyhydroxides, and (2) all trace elements are affected by processes that operate more strongly under low-oxygen conditions, e.g., Mn/Fe redox cycling, increased availability of organic carbon substrates, and presence of H$_2$S at sediment redox boundaries or in the water column under euxinic conditions (Pedersen & Calvert, 1990).”

At redox boundaries at sediment-water interfaces or within the sediments, elements (e.g. Fe and Mn) may transform between the dissolved and solid forms, which normally occurs within a relatively narrow redox cline (Stumm & Morgan, 1996).

In general, the formation of sulphides and preservation of organic matter are favoured by anoxic bottom water conditions during rapid sedimentation and burial (Berner, 1984; Pedersen & Calvert, 1990). During slow sedimentation rates, oxic conditions can be established. Although these conditions do not favour the precipitation of sulphides metals may still be available to diffuse through the oxic sediment and deposit in underlying anoxic sediments (Lyons et al., 2006). Trace elements commonly found within shales and basinal sediments include Al, Ni, V, K, U, Mo and Th (Jones & Plant, 1989). These trace elements are also commonly associated with organic matter, clays and can be used to determine to the anoxicity during sedimentation (Lyons et al., 2006). Moreover, they can be used as tracers for diagenetic fluids responsible for mineralisation and cementation (Hollis, 1996).

Carbonate production on the North Wales Platform and in the East Irish Sea Basin was limited from the Brigantian and was succeeded by the
deposition of pro-delta mud, which forms the Holywell Shales (Jerrett & Hampson, 2007). These Mid-Carboniferous (Namurian) shales from the East Irish Sea Basin are moderately enriched in V, Pb, Cu, Ni, Zn and Pb (lead), although horizons with low trace element concentrations do occur and suggest oxic bottom water conditions (Long, 2008). Combined with stable isotope data the overall conditions of deposition are considered to be anoxic (Armstrong et al., 1997).

3.7.1 Sulphur source

Sulphide mineralisation on the North Wales Platform requires a source of sulphur. Potential sources include formational fluids, basinal brines, H₂S produced during organic sulphate reduction, directly from hydrocarbon and/or from evaporites (Beales & Jackson, 1966; Anderson & McQueen, 1982; Coleman et al., 1989b). Based on the range of sulphur sources differing models for the transport of sulphur have been proposed by Sverjensky (1981) and Anderson & McQueen (1982). The first proposes a single flow model, where reduced sulphur is transported in the same fluid as the metals. Controls on this model include Eh, pH, temperature and pressure. The second model invokes metalliferous fluids interacting with a sulphur source within the host-rock limestone.

Sulphur Isotope data for the North Wales Platform is limited; values have been recorded from Llanrwst and Oswestry (and Shropshire) (Pattrick & Russell, 1989). The data indicate a contrast in δ²⁹⁸ values between the two locations, a spread between different minerals species but a narrow range for the same mineral species. It has been suggested that this is a result of different local sources of sulphur (Pattrick & Russell, 1989). Moreover, there are several generations of sulphide mineralisation, dated from the Ordovician to the Mesozoic (Fletcher et al., 1993; Haggerty & Bottrell, 1997). There is general trend from hydrothermal mineralisation, determined from fluid inclusion analysis, to a low temperature system with probable influx of δ³⁴S enriched, surface derived fluids (seawater/evaporative groundwater) (Haggerty & Bottrell, 1997). Mineralisation recorded around Llanrwst took place above 100°C.
suggesting that the sulphate reduction occurred via organic processes and became increasing enriched in $\delta^{34}$S (op. Cit.). The temperature reduction alone was considered insufficient to account for this enrichment and therefore a change in fluid composition is suggested. In addition, the reduction of sulphate mineralisation to sulphides has also been postulated (Haggerty & Bottrell, 1997).

3.7.2 Mechanism for metal, element and carbonate ion release and transport

A number of mechanisms for the release of trace elements and metals exist. These include clay diagenesis, membrane filtration, and alteration of high Mg to low Mg calcite and hydrocarbon maturation (Jackson & Beales, 1967; Coleman et al., 1989b). Currently, the most popular mechanisms for metal trace element release are the breakdown of clays (smectite-illite) and hydrocarbon maturation (Neilson & Oxtoby, 2008). The metals are then transported within basinal brines as part of a complex. Elements important within this study include Ca, Pb, Zn, Cu, F and Mg.

- Ca can be released to fluids by pressure dissolution, dissolution of cements or fauna, clay diagenesis, feldspar dissolution and/or dolomitisation (Morse et al., 2007).

- Pb (Lead), Zn, Cu within shales can be released from Pb sulphides, K feldspars, micas and organic complexes (Plant & Jones, 1989).

- F (Fluorine) can be released from organic matter, heavy minerals, Fe oxyhydroxides, Mn oxides, aluminosilicates, and during the stabilisation of high Mg calcite and aragonite (Hollis, 1996). Fluorine is often released slowly during burial (Fuge & Andrews, 1988).
There are several mechanisms for transport of metals and trace elements; these include inorganic and organic complexes such as chemo-metallic complexes, chloride complexes, and organo-metallic complexes (Sverjensky, 1981). Many of the mechanisms are still poorly understood but the most favoured is the chloride complexes due to its stability (op. Cit.).

3.7.3 Inorganic complexes
The role of inorganic complexes (F and Cl) in the transport of metals is considered to be an important factor during MVT/Pennine Style mineralisation on the Derbyshire Platform (Hollis, 1996). Although F-complexes were postulated as a transport mechanism, due to the large volume of fluorite mineralisation and ionic pairing possible with other elements, there was no correlation with other trace elements. Moreover, Cl and metals are considered to form more stable complexes (Giordano, 1996, 2002).

3.7.4 Organic complexes
Organo-metallic complexes are of increasing interest to studies regarding MVT mineralisation and hydrocarbons (Giordano, 2002). Although inorganic complexation can account for many processes related to metal transport, it is unable to fully account for lower temperature mineral deposits (50-200°C) associated with organic matter and basin diagenetic processes (Giordano, 1996, 2002). Moreover, many MVT deposits are intimately associated with hydrocarbon, have a similar fluid geochemistry to oil field brines and temperatures of formation that overlap with hydrocarbon maturation temperatures, thus, suggesting involvement of organic complexes (Parnell, 1988b).

Elements such as Cu and V favour complexation with organic ligands (Breit & Wanty, 1991). Organic ligands can form aqueous complexes with metals during diagenesis enabling mobilisation (Giordano, 1985). They also provide a source and sink for H+ ions, acting as a reducing agent to produce sulphides and also a control on pH that determines the
conditions for dissolution and precipitation (Giordano & Kharaka, 1994). The solubilities of trace elements and metals such as Ca, Mg, Fe, Al are controlled by redox states and pH and tend to be more soluble in organic acids than in fluids containing CO$_2$ (Giordano, 2002). Common organic aqueous complexes include acetic acid and organo-sulphur compounds although metals can also complex with organic matter (tetrapyrole complexes) (Parnell, 1990). The organic acids can be produced by decarboxylation and maturation of organic matter at elevated temperatures (~80°C) (Giordano, 2002). Little is known about tetrapyrole complexes although it has been noted that they tend to form more stable complexes with trace elements V, Ni and F (Parnell, 1990). Organic complexation has often been invoked as a mechanism for metal transport from hydrocarbon producing basins however, the importance of organic complexes remains an area of debate (Parnell, 1988b). The reducing nature of organic materials can act to inhibit co-migration with metals and where metal enrichment within organic material occurs can also inhibit the dissolution and remobilisation of other trace elements (e.g. Ca) and increase precipitation rates (op. Cit.).

Previous analysis of MVT deposits by Leach et al. (2005) have noted that there is generally a relatively significant spread in salinity values yielded from fluid inclusions. This is considered to be a result of fluid mixing, possibly during deposition, and the subsequent changes in pH and temperature would destabilise the complexes, releasing the metals for mineral precipitation (Neilson & Oxtoby, 2008).

3.7.5 Lower Carboniferous

Trace elements and metals for mineralisation on the Derbyshire and Askrigg Platforms were released from the Arnsbergian-Chokerian shales in the Edale Basin and Brigantian shales in the Craven and Widmerpool Basins during burial diagenesis (organic maturation and clay transformation, smectite-illite) (Hollis, 1996). The minerals deposits in the Pennine Orefield were precipitated from highly saline fluids (Heyl, 1969;
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Hollis, 1996). Fluid inclusion analyses from fluorite indicate NaCl dominated deep formational fluids analogous to oil field brines (Dunham, 1983). In addition, an NaCl-CaCl$_2$ brine with Mg$^{2+}$ contamination was detected from the eastern Derbyshire Platform margin in close proximity to the occurrence of dolomite (Hollis, 1996). The volume of hydrocarbon on the Derbyshire Platform (and Askrigg Platform) is negligible compared to the volume of Pennine Style and MVT mineralisation observed. Moreover, petrographic analysis suggests the hydrocarbon was emplaced prior to the main stage of mineralisation (op. Cit.). Inorganic complexing was more likely via Cl and minor F complexes (Hollis, 1996). Similarly to the Derbyshire Platform, Smith (1973) reported high salinities for MVT mineralisation in North Wales, derived from fluorite inclusion analysis. In the absence of evaporites within the Lower Carboniferous succession in North Wales the fluid composition suggests a basinal source (Smith, 1973; Davie et al., 2004).

Literature regarding the North Wales Platform suggests that hydrocarbon occurs as minor bitumen deposits (Parnell, 1983) which may suggest that there is potentially not enough hydrocarbon for organic complexing. However, the high salinities reported by Smith (1973) suggest that there may have been enough Cl for complexing, should the measured fluid salinities be reliable.

3.8 Faulting and fracturing in carbonates

The majority of the world’s remaining hydrocarbon resources are located within carbonate reservoirs (Moore, 2001). Fracture systems often dominate the permeability architecture of carbonate hydrocarbon reservoirs and aquifers (Cox, 2001). Therefore, the fracture networks are a major control on fluid flow and transport and understanding the parameters is crucial to reservoir and resource modelling (Zazoun, 2008).

3.8.1 Joints, faults and fracture networks

Joints, fractures and faults are discontinuities that are abundant within natural outcrop and form when the material loses cohesion and a result of
changing stress conditions (Twiss & Moores, 1992 and references therein). The term joint refers to generic structures (faults and fractures) (*op. Cit.*). Fractures are defined by their relative displacement across the fracture surface. Mode I, extensional or opening mode fractures are produced when mechanical failure occurs perpendicular to the fracture walls, mode II are a result of shear failure or sliding where failure is perpendicular to the fracture walls and mode III results from shearing parallel to the fracture edge. A combination of modes is termed mixed mode (*op. Cit.*) (Figure 3.8). Faults form from mechanical failure and shearing akin to mode II and mode III fractures although significant offset is observed. Similarly they also have a wide range of morphologies and associated damage zones that range in porosity and permeability (Aydin, 1978; Faulkner *et al.*, 2003).

Joints can be systematic or non-systematic depending on whether they are regularly arranged and linear or irregular with curved geometries. The similarity in geometry and orientation of joints can be grouped into joint sets. Stratabound joint sets terminate against bedding planes and tend to be fracture dominated. The beds themselves are said to be ‘decoupled’, resulting in separate joint systems occurring in adjacent layers that differ in properties. The joint spacing tends to be regular $C_v < 1$ and the lengths are limited (log-normal). Where there is more than one joint set present connectivity tends to be high and, therefore, permeability tends to be anisotropic in the horizontal (Odling *et al.*, 1999).

Non stratabound joint sets generally consist of fault and large fracture systems which have less of a contrast between horizontal and vertical permeability where the joints are open (Odling *et al.*, 1999). The joint spacings are a mixture of random to clustered $C_v \geq 1$ (*op. Cit.*). With increasing depth and overburden stress, through-going joints are favoured and, thus, stratabound joints are thought to be formed in shallower crustal environments (Twiss & Moores, 1992). Faults tend to form in a dominant orientation within a given area and so connectivity appears to be less than with joint systems due to fewer intersections.
between faults (Harris et al., 2002). However, fault swarms are the exception, creating a high density of highly connected lineaments. The high degree of clustering within fault zones tends to result in a coefficient $C_v > 1$ (Odling et al., 1999). Joints occur when the effective tensile stress is greater than the tensile strength of the rock (Twiss & Moores 1992). This can occur in a variety of situations that include overpressuring and tectonic activity (op. Cit.).

Figure. 3.8. Fault and fracture modes, A) Mode I, opening mode, B) Volume loss during compaction and stylolite formation, C) Model II, in plane shear, D) Mode III, out of plane shear. $1-3 = \sigma$ stress directions, 1 is the maximum stress and 3 is the minimum stress.
3.8.2 Controls on fault/fracture distribution

Fracturing is controlled by the subcritical crack index and the elastic properties of the host rock (Atkinson, 1982; Olson, 1993). These properties are dependent on grain size, sediment composition, porosity, bed thickness and superimposition of diagenetic processes (Gross et al., 1995; Eberli et al., 2003).

Brittle lithologies are more prone to fracturing these are generally but not exclusively composed of fine grained and/or well cemented sediments. It has also been illustrated that thinner beds are also more likely to host fractures (Hobbs, 1967, Twiss & Moors, 1992). On a larger scale facies variation and sediment stacking patterns, dictated by the environment of deposition, will control the development of fractures through a succession (Di Naccio et al., 2001). A succession can therefore be divided into units based on their mechanical properties, which can vary on a sub-bed to bed scale and bedding planes often behave as mechanical boundaries (Gross, 1995). The study that encompasses the controls on mechanical rock properties is often referred to as the mechanical stratigraphy (Eberli et al., 2003; Gross et al., 2005). Mechanical stratigraphy and the overall intensity of deformation depend upon the rheology of the rock and applied stress that is intrinsically related to lithology, diagenesis, P/T and strain (McQuillan, 1973; Odling et al., 1999; Gross, 2003). There is a link between the controlling factors and improving our understanding of this is crucial to characterising fluid flow within carbonate reservoirs (Di Naccio et al., 2001).

3.8.3 Fluid flow around fault zones

When trying to understand the controls on fluid flow and the distribution of hydrocarbon and mineralisation related to faults and fracture systems it is important to consider the permeability across fault zones. This is especially true in carbonates when early diagenesis has significantly modified the host-rock primary porosity and permeability thus resulting in the faults and fractures acting as the dominant pathways (Townend &
Zoback, 2000) or conversely, acting as a permeability barrier (e.g. Blanpied et al., 1992).

Fault zones are normally comprised of a fault core and a surrounding damage zone (Figure 3.9) (Aydin, 1978). The fault core carries the greatest displacement and consists of fine grained material such as cataclasite and gouge resulting in a low permeability zone (Byerlee, 1990). The damage zone normally comprises brittle fracturing (mode 1), brecciated host-rock and/or localised folding (e.g. drag folds), has less displacement and is often more permeable (Kim et al., 2004). In addition, the damage zone can locally include secondary slip surfaces and/or areas of pressure solution (stylolitisation) (Bazalgette pers. Comms. 2010). Permeability within a damage zone is significantly reduced when the fractures become occluded by fine grained matrix related to continued deformation or by cements and mineralisation related to fluid flow. The fault zone structure and pattern of deformation can vary in style, connectivity and lateral/vertical extent (Faulkner et al., 2003). The result depends on the rock properties and the behaviour of the faults (Smith, 1966; Jones et al., 1998).

The internal architecture of fault zones has long been known as a major control on fluid flow within the crust (Caine et al. 1996). An understanding and ability to predict the structure would have major implications for characterising and modelling faulted hydrocarbon reservoirs and exploration of economic mineral deposits. Therefore, an increasing number of studies have been employed to try and understand and characterise fault zones and associated diagenesis (e.g. Caine et al., 1996; Tarasewicz et al., 2005; Woodcock et al., 2006, 2008; Mitchell, 2007).
3.8.4 Mechanical stratigraphy

This section briefly outlines the concept of mechanical stratigraphy. Throughout this study the control of lithology and facies on rock properties is mentioned. While it is not the focus of the study to look in detail at the mechanical stratigraphy it is an important concept to consider when analysing the distribution of fault and fracture networks and is imperative when modelling or predicting such systems (e.g. Van Gent et al., 2009).

Mechanical stratigraphy can occur at a variety of scales from regional where different lithologies can deform differently under the same stresses, down to a bed and sub-bed scale where sedimentary interfaces (bedding planes) and/or variation in facies (composition, grain size, porosity) and cementation can be the dominant controls on fracture initiation and propagation under given loading conditions (Welch et al., 2009). These
controls evolve through time and therefore current day mechanical units and measured mechanical properties do not necessarily represent those at the time of deformation (Rutter pers. Comms. 2010).

3.8.5 UK Regional stress regimes
Many local fault and fracture networks are controlled by regional deep seated structural trends. These trends are often reactivated during subsequent tectonic episodes (e.g. Caledonian and Variscan compression) (Fraser & Gawthorpe, 1990). Therefore, the regional stress regimes must be taken into account when fully assessing the controls and timing of local scale deformation and basin evolution. A summary of the UK regional stress regime and structural trends is detailed below.

Rifting during the Lower Carboniferous followed arcuate Caledonian trends with NW-SE orientated extension within onshore UK basins and the North Sea (Coward et al., 2003). Fraser & Gawthorpe (1990) recognised, from stratigraphic and sedimentary analysis, two phases of rifting and a number of smaller pulses within the Lower Carboniferous of northern England during the early Chadian and Visean. In addition, they recognised N-S fault trends. As a result of the differing fault trends documented throughout the UK it has been suggested that extension occurred in a north-south direction. However, Coward (1993) proposed that a simple extensional model could not account for all the trends observed and suggested that right-lateral shear was more likely.

The Variscan Orogeny occurred across the south of England through to mainland Europe throughout the Carboniferous, with basin inversion initiated in the late Carboniferous (Westphalian to Stephanian; Corfield et al., 1996). North Wales was peripheral to these tectonic movements resulting in only minor folding, faulting and fault reactivation of Caledonian trends (NE-SW and N-S lineaments). A second phase of tectonic activity, the Alpine Orogeny during the Tertiary, also reactivated
faults within North Wales but this time with a more east-westerly trend (Wilson, 1968; Reedman, 1984). Between the end Permian and Cretaceous, North Wales was affected by the regional NW-SE orientated rifting related to the opening of the Atlantic, which resulted in regional, NE-SW trending normal faults (Chadwick & Evans, 1995; Coward et al., 2003). It is difficult to accurately determine the nature of post-Jurassic deformation as post-Jurassic sediments are absent from onshore North Wales and the adjacent Cardigan Bay Basin (Tucker & Arter, 2003) and Cheshire Basin (Lewis et al., 1992, Smith, 1999). Only in the East Irish Sea Basin have minor Cretaceous sediments been recorded (Floodpage, 2001). The widespread absence of these units is considered to be a result of Late Cretaceous-Tertiary (Alpine) NW-SE trending inversion (Tucker & Arter, 1987; Lewis et al., 1992; Floodpage, 2001). This is consistent with the latter phase of fault reactivation and change in principal stress direction observed within the Conwy Valley System (Shackleton, 1953) and on the Great Orme.

Following Tertiary inversion, the UK was subject to pulses of NE-SW orientated extension and volcanic dyke emplacement (Coward et al., 2003). During this period, North Wales was still a region of emergence with limited tectonic activity (Davies et al., 2004)

### 3.8.6 Lower Carboniferous faults and fractures

Lower Carboniferous structures include faults, fractures and folds. North Wales and NW England have for the most part been situated peripheral to major tectonic events and major structural deformation. Therefore, successive structural episodes have never completely overprinted evidence of earlier episodes (Davies et al., 2004).

The internal architecture of faults is commonly described within geological study but has yet to be fully understood in terms of process of formation and the implications for fluid flow (Sibson, 1989; Woodcock et al., 2007). Recent studies by Tarasewicz et al. (2005) and Woodcock et al., (2006, 2007) address this topic using examples from the Dent Fault, NW
England. The Dent Fault is one of a number of UK basement lineaments that were reactivated during the Variscan Orogeny and subsequent tectonic episodes (Woodcock et al., 2006). The Dent Fault and adjacent sub-parallel faults displays elements of sinistral strike-slip, reverse and dip slip movement along their lengths and are associated with monocline folding (Woodcock et al., 2008). The internal architecture generally consists of 1-10cm fault cores comprising cataclasite and fault gouge and 10-100m brecciated damage zones displaying chaotic and fitted fabrics (op. Cit.). Similar mixed mode faulting and internal architectures have also been recorded in North Wales (Nichols, 1968; Wilson, 1968; Tremlett, 1970; Bassett, 1984; Lee et al., 1990; Williams & Eaton, 1993).

3.8.6.1 Distribution
Faulting and fracturing appears to be distributed differently between platforms in North Wales and England. Structure on the North Wales Platform is located around pre-existing Caledonian lineaments such as the Bala Lineament and half graben structures initiated during Lower Carboniferous extension and reactivated during Variscan compression (Fitches & Campbell, 1987; Gawthorpe et al., 1989). Structure on the Askrigg Platform is similarly situated close to large structures such as the Craven Fault. However away from these large structures, fault and fracture networks are less well developed these regions have previously been referred to as a ‘structural plateau’ (Dunham & Wilson, 1985; Hollis & Walkden, 2012). Whereas the Derbyshire Platform displays better developed faults and fracture systems evidenced by widespread mineralisation associated with fluid flow during deformation in the Late Carboniferous and early Permian (Hollis & Walkden, 2012).

3.8.6.2 Structure on the North Wales Platform
Situated on the southern periphery of the Pennine Basin during the Early Carboniferous, with major compressional belts to the south/south-east during the late and post-Carboniferous, the North Wales Platform was subjected to multiple phases of faulting and folding into the Tertiary

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(Fraser & Gawthorpe, 1990; Turner 1997). The structures observed across the North Wales Platform follow predominantly Caledonian trends (NE-SW and an E-W structural grain) (Nichols, 1968; Wilson, 1968; Tremlett, 1970; Bassett, 1984; Lee et al., 1990; Williams & Eaton, 1993). Major structural systems in North Wales include the Menai Straits Fault System, a Caledonian shear zone, bounded by the Aber-Dinlle Fault to the south and the Dinorwic Fault to the north, the Clwyd Half Graben, Alyn Valley Fault System and Bala Lineament. These major faults have been active since the Cambrian and/or Devonian. The systems display extensional – transtensional components with evidence of both normal and strike-slip movement (Tremlett, 1970; Reedman et al., 1984; Williams & Eaton, 1993; Figure 3.2).

The Conwy Valley Fault System is a network of NE-SW trending faults (Figure 3.10) that were active from the onset of the Caledonian Orogeny (Tremlett, 1970; Campbell et al., 1985). It originated as a strike-slip system, which was later reactivated with normal movement (Reedman et al., 1984; Woodcock, 1988; Gibbons, 1990). Adjacent fault systems in North Wales such as the Alyn Valley and Nercwys-Nant-Figillt (Flintshire) fault systems display similar trends and evidence for activation and contemporaneous movement with the Conwy Valley faults (Davies et al., 2004). Between the major faults (Aberdinlle, Dinorwic and Berw Faults) within the Conwy Valley System, subsidiary faults have developed. The faults are up to 5km in length and are orientated perpendicular and conjugate to these major faults, observed on the Great Orme (Nichols, 1968) (see chapter 6). To the east of the Great Orme, the Gloddaeth Syncline and the Clwyd Fault System (Waters & Davies, 2004) both display extensional – transtensional components with associated strike-slip subsidiary faults (Tremlett, 1970; Reedman et al., 1984; Williams & Eaton, 1993; Figure 3.10).

The fault systems active in Flintshire during the Carboniferous are orientated N-S and NNW-SSE and are predominantly dip-slip, although component of strike-slip have been observed (Campbell & Fitches, 1987; Gawthorpe et al., 1989; Davies et al., 2004). Growth faulting and
3.9 Structural diagenesis

Structural diagenesis is the combined analysis of structural and diagenetic processes in order to determine the timing and development of fracturing and fluid flow and associated modification of the mechanical
rock properties (Laubach, 2000; Gale et al., 2004). This relatively new subject area has recognised the intimate relationship between mechanical characteristics of a rock and the diagenetic history and in particular the development of fracture networks. Assessing the geometric characteristics of fractures alone is unreliable for determining the controls on their distribution and density (op. Cit.). Moreover where complex diagenetic processes occur, the mechanical rock properties can vary widely through time and overprinting can destroy textures diagnostic of fracture initiation, growth and early diagenetic phases (Ortega et al., 2010).

Structural diagenesis was initially employed to investigate the timing of fracturing and cementation within siliclastic lithologies. More recent studies have focused on fracture development within dolomites. The increasing interest has been driven by the petroleum industry. Many of the world’s reservoirs are hosted by dolomite (Braithwaite et al., 2004). Where dolomitisation has resulted in unfavourable characteristics, reduction in porosity and permeability, fractures can act as the primary conduits for fluids. Dolomitisation often destroys host-rock textures making it difficult to determine diagenetic processes prior to alteration. Analysis includes characterising fracture morphology, distributions, cross-cutting relationships and fracture fill at a variety of scales. Field studies can range from regional, kilometre scale down to sub-millimetre scale. Comparatively subsurface studies predominantly rely on limited data and micro-scale structures within core. A number have studies have tackled the issue of scale and many indicate that micro-structures can be extrapolated to the macro-scale (Marrett et al., 1999).

Another difficulty with structural diagenesis is with differentiating the timing of fracturing and the timing of fluid-flow and cementation within the fractures. Fracture fill textures can be indicative of syn-kinematic (during fracturing) and/or post kinematic cementation (Laubach, 2000). Bridging, fibrous and syntaxial cements with crack-seal textures are typical of syn-kinematic precipitation whereas blocky, drusy and heterogeneously distributed cements are typical of post kinematic passive fracture fills
(Laubach, 2000, 2003). The texture of the fracture fill is further controlled by rates of fracture opening, fracture aperture, fluid flow rates, volumes and geochemical constraints (op. Cit.). Although flow rates may influence the sealing of fractures by post kinematic cements, high flow rates and pressures are more likely to influence fracture initiation and growth during syn kinematic periods (op. Cit.).

Structural diagenesis has been successfully employed as a tool for determining the relative timing of fracture events and fluid flow (Marquez & Mountjoy, 1996; Montanez, 1997). By understanding the rock properties responsible for the initiation, growth and sealing of fractures using structural–diagenetic parageneses, the subcritical crack index (see above) can be used to calibrate models and predict fracture networks (Rijken et al., 2002; Gale et al., 2004). Although this methodology has been widely accepted as a means of understanding fracture and fluid flow, caution has been urged (Mitchell, 2007). Models for fracture geometry and prediction are location and control specific thus field studies need to take into account the burial history of the rocks and the variation in local and regional stresses through time.

### 3.10 Summary and key topics

- Diagenesis is an important controlling factor regarding the development and destruction of porosity within carbonate platforms and thus is an important part of palaeo-fluid flow study and reservoir analysis. Using the super-position and cross-cutting relationships of diagenetic features a relative timing of these events can be determined. On the North Wales Platform previous studies have focused on early diagenesis (marine, meteoric and shallow burial environments) with little attention paid to deeper burial diagenetic processes and products.

- Dolomitisation is a diagenetic process that has received increasing attention driven by industry and academic interest. Dolomitisation
can enhance or destroy porosity and permeability within carbonates. Dolomitisation on the North Wales Platform has received little attention within previous diagenetic studies and further study can provide insight into fracture related dolomite.

- Mineralisation including MVT and Pennine Style form economically important deposits within northern England and Wales. The spatial and temporal relationship of the mineralisation to cement phases (e.g. calcite and dolomite) and composition can indicate the timing of major episodes of trace element/metal release and fluid migration, source and flow pathways.

- Understanding palaeo-fluid flow can help to understand basin development and porosity and permeability evolution within carbonate systems. It also has relevance to current day carbonate systems such as determining suitable subsurface areas for waste and water containment.

- Trace element and REEs can be sourced from sediments during burial and diagenesis and can be easily transported in fluids or complexes before being incorporated in cements or minerals. Therefore, trace element and REE analysis in combination with standard stable isotope techniques can provide a robust dataset and tracers to help determine the source and fluid flow pathways of diagenetic fluids (e.g. Hollis & Walkden, 2002).

- Structural diagenesis is a relatively new area of research. The combined study of structures and the cements that they host can enable a more robust determination of the timing of fault/fracture activation (fluid follow pathways) and/or fluid flow. The technique has already been employed with success and may provide further constraint on the structural evolution of the North Wales Platform.
Chapter 4: Methodology
Chapter 4

4.0 Methodology
The study employs a multi-scale, interdisciplinary approach which includes complementary sedimentological, petrographic, geochemical, isotopic and structural analysis. A variety of fractured platform margin and platform top sediments of Dinantian age were recorded and sampled. The interval of interest (Dinantian) was used in order to compare and contrast the diagenetic and burial history with well documented adjacent and contemporaneous carbonate platforms (e.g. Derbyshire, Askrigg Platforms).

4.1 Study sample locations
A sedimentological, structural and diagenetic evaluation was conducted across the North Wales Platform. Over 200 rock samples were collected from natural and quarry exposures over an area of ~45km².

A series of transects (13) were conducted along well exposed outcrop and across faults and fracture systems, from the Great Orme, Little Orme, Prestatyn, Halkyn, Minera and Llangollen (Figure 4.1).

Figure 4.1. Map of the study area displaying the main sample and logging/transect locations, North Wales. Be: Berw Fault, D: Dinorwic Fault, AD: Aberdinlle Fault, CV: Clwyd Valley Fault.
4.2 Field methods
Sedimentary logs were recorded. Each log detailed (see Appendix) In addition, transects or scanlines were recorded from 13 locations. The transects vary in platform position and stratigraphic level in order to record spatial and temporal facies changes and geochemical variations. Pore-occluding cements and matrix replacive mineralisation were recorded to try and document distributions across the platform. Transects conducted perpendicular to orientated and documented fault and fracture systems were logged and sampled in order to assess facies controls on fracture network development, geochemical variations/evolution along structures and the extent of fluid-rock interaction laterally away from structures. Samples collected were orientated. The cements and mineralisation within and adjacent to the fault/fracture systems are key to constraining the development of these fluid flow pathways, timing of reactivation and evolution/destruction of porosity.

4.3 Laboratory analysis
4.3.1 Transmitted light microscopy
Some 150+ polished and standard thin sections were produced from representative host-rock limestone, vein cements, mineralisation, and dolomite samples. The sections were cut from orientated samples and half carbonate stained a further subset of 20 polished and standard thin sections were impregnated with blue resin in order to visualise the porosity within the dominant facies from each formation under investigation (see chapter 5). The sections were viewed under transmitted light techniques using a Nikon and Laser Optik System.

4.3.2 Cathodoluminescence (CL)
CL techniques were used to define and quantify discrete cement phases and assess cross-cutting relationships, forming the basis for a paragenetic framework. CL is conducted by bombarding a polished
section with electrons. The compositions of minerals are thought to control the luminescence, elements hosted by the carbonates either activate or quench luminescence and further influence the resulting characteristics such as colour. The main activator within carbonates has been attributed to presence of Mn$^{2+}$ although rare earth elements (REEs) such as Eu$^{2+}$, Eu$^{3+}$ and Sm$^{3+}$ exert a minor influence. In contrast, Fe$^{3+}$ and Ni$^{2+}$ are some of the ions that behave as a quencher. Cathodoluminescence was achieved using a Cambridge CCL cold luminoscope 8200 mk3, operated at an accelerating voltage of 10Kv, a vacuum of 2 torr and a gun current of 300Kv. Photographs were taken using a Progres C10 Laser Optik System.

4.3.3 Scanning electron microscopy (SEM)
SEM was employed to investigate the potential for crystal zonation that was not evident with transmitted light or CL techniques. SEM analysis was conducted using the JEOL JSM-6400 SEM with Princeton Gamma Tech EDX system in backscatter mode using 25-30 µm thick polished sections. The SEM was operated with at a pressure of 3.7e-6 mBar, 15Kv and with a beam size of 5µm.

4.4 Geochemical methods

4.4.1 Staining
160 30µm thick polished sections were prepared and half stained with alizarin red S and Potassium ferricyanide following Dickson (1965). The staining is carried out in order to distinguish between ferroan and non-ferroan calcite and dolomite. This provides the basis further investigation and interpretation.

4.4.2 X-ray diffraction (XRD)
XRD was carried out in order to determine the constituent components of the carbonate and/or cements under investigation. It is also used to indicate the degree of order within dolomite phases. XRD operates by
analysing the angles of X-ray diffraction after hitting the samples. The X-rays are generated by bombarding a Cu anode with high-energy electrons. X-rays are then emitted and directed at a rotating sample. The output displays the intensity of the diffracted peaks, which can then be compared with standard peaks to determine the composition.

30 powdered samples were acquired using a precision drill for analysis. These were then prepared following the methodology of (Charlier et al., 2006). The analysis was carried out using a Bruker D8Advance diffractometer within the University of Manchester. A tube voltage of 40 kV and a tube current of 40 mA, with a step size of 0.02° and time constant of 2.00 s was employed, using copper k alpha 1 radiation. During each XRD analysis, a thin smear was prepared by mixing approximately 0.5 g of the powdered sample with a few drops of amyl acetate and then leaving it to dry on a small glass slide. This was then inserted in the diffractometer. Semi-quantitative estimations of bulk mineralogy fractions were carried out using peak area measurements (sensu Schultz, 1964). All results contain an analytical error of 0.05. Alignment was regularly checked against an internal quartz standard during the analyses.

4.4.3 Major and trace elements

Major and trace elements can occur within minerals, at crystal boundaries and between lattice planes. Trace elements can be incorporated into the crystal lattice by solid substitution, where elements of similar ionic radius and charge can replace host ions, fluid or mineral inclusions, occlusion in lattice defects or sorption onto crystal surfaces (McIntire, 1963; Banner, 1995). The partitioning of a trace element from a liquid phase into a solid lattice phase can be quantitatively represented and predicted using the distribution coefficient ($k_D$). A trace element coefficient of $<1$ discriminates against the incorporation of the trace element into the mineral phase, and a value of $>1$ indicates preferential incorporation of the trace element (Banner, 1995). However, the experimental determination of $k_D$ values for dolomite yield a wide range and so trace element analysis is often used
to gain only general information on the nature of the diagenetic fluids (Brand & Veizer, 1980; Machel, 1988).

*In situ* Major and trace element analysis was carried out using ICP- AES, electron microprobe and TOFSIMs ion microprobe. The analysed elements include Fe, Mg, Mn, Ca, Sr, Al. Further, analysed elements were selected because of their association with mineralisation and with burial including cementation Cu, Pb, Zn, Na and Rb were also analysed. ICP analysis was conducted using powdered samples of host rock limestone and isolated dolomite phases. Powdered samples were treated with 6M HCl for 24 hours to digest the carbonate phases. An aliquot containing 10 ml of solution was then transferred to an ICP vial. Corresponding samples were drilled from hand specimens and their purity checked where necessary by XRD techniques. Trace element concentrations were measured using a Perkin-Elmer Optima 5300 dual view ICP-AES with reproducibility of 0.1‰ (1σ).

Electron microprobe and Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) analysis were carried out using 25µm, unstained polished sections, which were carbon coated prior to analysis. Trace element concentrations were measured using a Cameca SX 100 Electron Microprobe. Operating conditions: accelerating voltage of 15Kv, beam current of 20nA, beam size of 5 µm or 10µm and internal standards were used for calibration. TOF-SIMS was operated using a gold beam, emitting Au+ ions, ~1nA direct current, 25keV focused to a <1micrometer spot. The beam was operating with ~20ns pulses that rastered across the sample. Mass resolution was ~3000 mass resolving power. Total secondary ion maps of the analysed area were used to define areas for detailed study. Mass resolved images and quantitative elemental abundances were then obtained. TOF-SIMS was conducted following the methodology of King *et al.* (2009).

A wollastonite standard was used for the electron microprobe analysis.
4.4.4 Stable isotopes (0/C)

Stable isotopes analysis (oxygen and carbon) has been employed to characterise discrete cement phases and to help determine the composition of the parent fluid and extent of diagenetic alteration following initial precipitation. Isotopes of the same element differ in mass and energy. Where more than one isotope occurs, the lighter of the two isotopes is more reactive. The change in ratio of the two isotopes during chemical reactions (e.g. cement precipitation) is referred to as fractionation. Moreover, each reaction can be defined by a temperature dependent fractionation coefficient (Emery & Robinson, 1993). Abundant stable isotopes with suitable differences in relative masses to enable detection include $^{16}$O, $^{18}$O, $^{12}$C and $^{13}$C. Stable isotopes are widely applied to carbonate diagenesis studies as they can provide information about the conditions during cement precipitation e.g. temperature. The controls on isotope composition, especially oxygen, include composition of the parent fluid and the fractionation coefficient between a fluid and solid. The alteration from the parent fluid signature can be used to discriminate between fluids sourced from different environments (i.e. marine, meteoric or burial) and also the extent of diagenetic alteration (Tucker & Wright, 1990; Hoefs, 1997).

In contrast to oxygen, carbon ($\delta^{13}$C) requires fluid-rock interaction or a change in fluid composition/source to alter the isotopic signature (Emery & Robinson, 1993). $\delta^{13}$C can provide an indication of meteoric fluids and soil derived CO$_2$ or CO$_2$ generated during maturation of organic matter. Within this study, orientated samples selected for stable isotope analysis consisted of whole rock limestone and dolomite and isolated diagenetic phases from fractures and the walls of interparticular and secondary porosity. The samples were chosen based on their diagenetic phase, host rock lithology, stratigraphic position and fracture orientation. The diagenetic phases and composition of the rock samples were determined by XRD and first pass transmitted light and CL petrography. Whole rock samples were chosen based on their dominant composition (e.g. dolomite
or calcite). Partially dolomitised limestones were not analysed due to a potentially large error associated with the correction. In order to reduce cross-contamination from adjacent diagenetic phases or host-rock, samples with one or two diagenetic phases and a simple cross-cutting relationship were identified and drilled using a 0.05mm drill bit. In addition, the rock sample was cleaned between collection of each powder sample using pressurised air and deionised water and the drilled bit cleaned using 0.5% HCL.

Stable isotope-analysis was conducted at the University of Liverpool. Powdered samples (4.5 mg) of host rock and discrete cement phases were acquired using a tungsten-tipped precision drill. Samples of calcite were reacted (to completion) with phosphoric acid under vacuum, at temperatures of 25 °C (McCrea, 1950). Gases were measured by dual-inlet, stable isotope ratio mass spectrometry using a VG SIRA10 mass spectrometer. Isotope ratios were corrected for $^{17}$O effects following the procedures of Craig (1957). Oxygen isotope data were adjusted for isotopic fractionation associated with the calcite-phosphoric acid reaction using a fractionation factor ($\alpha$) of 1.01025 (Friedman & O'Neil, 1977). Samples were run against an internal standard and all results were reproducible to $+0.1\%$O (2σ). All data is reported relative to the PDB standard.

The results have been interpreted using the oxygen fraction factor of Friedman and O'Neil (1977) for the calcite cements and Land (1983) for the dolomite phases.

\[
1000 \ln \alpha \text{ (calcite - water)} = 2.78 \times (106T-2) - 2.89
\]

\[
1000 \ln \alpha \text{ (dolomite - water)} = 3.14 \times (106T-2) - 2.00
\]

4.4.5 Rare Earth Element analysis (REE)

Rare earth elements in seawater are most commonly derived from the upper-crust (McLennan, 1994). Controls on incorporation of REE’s
include redox reactions, fractionation and partitioning (temperature), competition, fluid composition and bio/diagenetic influences (op. Cit.). REE analysis is often utilised during diagenetic studies in order to better constrain the fluid source(s) for precipitation. REE’s are relatively stable and therefore are considered to represent the composition of the precipitating fluid. Similar to carbon isotopes, modification of REE’s occurs during alteration under increased temperatures (diagenesis) and high water: rock ratios. Therefore at low temperatures, in order to modify the REE patterns water rock ratios need to be in the order of \( \geq 10^5 \) (Banner, 1988). In addition to characterising the fluid composition, the abundance, fractionation and anomalies indicates the mode of crystallisation and the physio-chemical environments which the fluids encountered (Bau & Moller, 1991). These details are invaluable when determining the fluid flow pathways.

Seawater signatures are characterised by ‘flat roof’ trends where there is no enrichment between the LREE’s and the HREE’s, with a prominent negative Ce anomaly. Negative Ce anomalies are common within natural waters such as seawater and fluvial water (Elderfield et al., 1990; Bau & Moller, 1991). The negative anomalies within normalised REE patterns are a result of valency changes compared to that of its neighbouring ions. Within natural systems the valency changes are controlled by redox reactions and Ce anomalies indicative of oxidising, low temperature conditions (Haley et al., 2004; Bau & Moller, 1991).

Fluids with elevated temperatures are characterised by REE patterns that display a lack of negative Ce anomaly, enrichment in HREE’s and where volcanic material is involved an Eu anomaly. In hydrothermal systems HREE enrichment compared to LREE’s can occur where the environment if slightly alkaline and of moderate temperature (130°C). Due to the presence of the ligands \( \text{CO}_3^{2-} \) and \( \text{OH}^- \), which form stronger complexes with the HREE’s preferential desorption of HREE’s results in enrichment in the solution (Bau & Moller, 1991). Thus pH is a controlling factor in REE transport and inclusion during precipitation. There is also a potential mineralogical control related to ionic radius, charge and bond. Due to the
differences in ionic radius between REE’S, Mg, Fe and Ca all REE’s co-precipitate with Ca minerals but LREE’s are preferentially rejected in Mg and Fe rich minerals e.g. siderite. The smaller HREE’s with higher ion charges are more readily incorporated in to the mineral lattices (Morgan & Wandless, 1980; Bau & Moller, 1991).

There is expected to be a depletion of the absolute REE values from sedimentary carbonates through to burial cements even if the negative Ce anomaly is preserved. Alternatively, if the precursor carbonates had been low in REE’s then an enrichment pattern in MREE’S and to a lesser extent HREE’s can be a result of later alteration and fluid:rock interaction. Within this study REE + Y analysis was carried out in order to further constrain the source of the fluids responsible for the different dolomite phases. Samples were selected that represent each dolomite phase base on petrographic and stable isotope analysis. Due to the sample size required (50-100mg) diagenetic phase separation and repeat analysis was not possible for all samples.

Powdered samples of host-rock limestone, bulk dolomite and individual cement zones were digested in 2ml of 20% HCl before dilution to 2% HCl. In addition, two blank samples were prepared in the same way for reproducibility. Corresponding samples were drilled from hand specimens and their purity checked where necessary by XRD techniques. REE’S and Y concentrations were measured using ICP-MS with an Agilent 7500cx mass spectrometer. Samples were run against internal standards and reproducibility of 0.1‰ (1σ). All samples are reported in mg/l or ug/l (ppm or ppb). All REE results have been PAAS normalised following the methods of Nance & Taylor (1976).

4.4.6 Strontium Isotope analysis (Sr)

Strontium isotope analysis is being increasingly employed within diagenetic studies and can provide additional constraint on the source of the fluids responsible for precipitation. Sr can be derived naturally from seawater and incorporated during carbonate production or it can be provided post-deposition through re-equilibration with Sr enriched
diagenetic fluids. $^{87}\text{Sr}$ and $^{86}\text{Sr}$ are relatively heavy isotopes and as a result are less readily fractionated during diagenesis compared with the stable isotopes and thus retain the Sr isotopic signature of the parent fluid. $^{87}\text{Sr}$ is derived from the radioactive decay of $^{87}\text{Rb}$, which in turn is commonly found within siliclastic sediments.

Powdered whole rock and discrete dolomite cements were obtained using a tungsten-tipped micro-mill following the methodology of Charlier et al. (2006) and Pollington & Baxter (2011). Sample purity was checked where necessary by XRD. Sr (Oak Ridge $^{84}\text{Sr}$, 1.1593ppm) and Rb spikes were added to each sample to boost the signal.

Strontium was extracted from the rock powders for isotopic analysis using Sr Spec extraction chromatographic resin. Column preparation and chemical separation were conducted following the methodology of Deniel & Pin (2001) and Charlier et al. (2006). Prior to analysis the Sr samples were mixed with Tantalum (Ta) emitter solution, loaded on to single Rhenium (Re) filaments and subjected to a 2A current. Sr isotope ratios were measured on the British Geological Survey (NIGL) Thermo-Finnigan Triton TIMS instrument in static collection mode. An internal NBS 987 standard was used for calibration with a reproducibility of $+0.1\%\text{_{o}}$ (2σ). During TIMS analysis spiked samples are run in the same fashion as unspiked samples. However, the results of spiked samples needed to be corrected, off-line, for spike contribution using standard techniques (op. Cit.). All results are reported to the NBS 987 standard.
Chapter 5: Sedimentation and Diagenesis on the North Wales Platform
Chapter 5

5.0 Sedimentation and diagenesis on the North Wales Platform, UK

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Abstract

The Lower Carboniferous North Wales Platform is located less than 20km from the hydrocarbon producing East Irish Sea Basin and includes the North-east Wales Orefield. Comprising Asbian and Brigantian strata, the area has undergone little to no study since the 1980’s and lacks published data regarding the diagenetic history. Detailed diagenetic study could provide better constraint on the conditions of deposition, porosity evolution and the occurrence and distribution of mineralisation. Through integrated, multi-scale, field and petrographic analysis a detailed sedimentary evaluation and paragenetic framework has been developed and compared with that of the adjacent, age-equivalent Derbyshire Platform. The data provides important information regarding fluid migration and porosity evolution within the Lower Carboniferous platform setting. Outcrops consist primarily of platform-margin facies; metre-scale upward-shallowing cycles that comprise skeletal wacke-packstones with thin interbedded mudstone units and capped by emergent surfaces and/or calcretes. Early diagenesis is recorded by pervasive marine and meteoric calcite cements occluding matrix porosity and syn-depositional
Chapter 5. Sedimentation and diagenesis

fractures. Consequently, several generations of burial diagenetic cements, calcite and dolomite, are mainly restricted to fractures. Evidence of telogenesis is recorded by burial diagenetic product post-dated by meteoric calcite cements, which occlude any remaining secondary porosity.

Overall, the diagenetic history of the North Wales Platform displays similarities to the Derbyshire Platform, but records a more complex paragenesis. This has largely been attributed to the different burial histories of the two platforms, and different fluid sources. Ultimately, the study provides a framework for prediction of diagenetic processes and product, and understanding the spatial and temporal relationships between structural deformation, sedimentation and diagenesis within a syn- and post-rift basin.

5.1 Introduction

Understanding and predicting porosity evolution and fluid flow pathways in carbonate platforms has long been a key challenge within diagenetic studies. However, individual studies often concentrate on one aspect of the diagenesis resulting in a limited understanding and uncertainty regarding the timing and controls of diagenetic events. In order to gain a full understanding of porosity evolution, multiscale, interdisciplinary datasets are required. In this context, outcrop studies represent unique datasets that allow 2D and pseudo-3D visualisation of the interplay between basin evolution and structure, facies distribution and diagenesis. Understanding the interplay of these large-scale elements in controlling patterns of porosity preservation, generation and destruction can help to reduce uncertainty in the subsurface geological models that are used to predict reservoir properties during exploration, appraisal and field development in the hydrocarbon industry. Within the UK, the Lower Carboniferous of the Pennine Basin has long provided such a framework for academic and industrial research (e.g. Fraser & Gawthorpe, 2003; Hollis & Walkden, 2012 and references therein). Studies by Gutteridge (1987, 1991), Hollis (1996) and Hollis & Walkden (2002, 2012) have
produced a comprehensive and well constrained paragenesis for the Derbyshire Platform, with some comparative work on the southern margin of the Askrigg Platform (Hollis & Walkden, 2012) and the Lake District (Horbury & Adams, 1989). Complementary studies focusing on the mineralisation of Northern England and Wales were carried out by Ixer & Vaughan (1993) and Pattrick & Russell (1989). Similarly, Wilkinson (2003, 2005) and Shelton et al. (2011) have produced detailed paragenetic studies for the age equivalent succession on the Isle of Man and Southern Ireland.

In comparison, the paragenetic history of the Lower Carboniferous succession on the North Wales Platform has not been fully described. Previous studies have focused upon sedimentological (Warren et al., 1984; Davies et al., 2004; George et al., 1976) and paleontological description (Neaverson, 1930, 1935, 1937; Bancroft et al., 1986; Davies et al., 1989, 2004; Somerville & Strank, 1984a, b; Somerville et al., 1989). In addition, the North Wales Platform hosts a variety of mineralisation including copper-iron, lead-zinc-barium and minor volumes of fluorite (Lewis, 1994, 1996; Ixer, 1996; Pattrick & Russell, 1989; Bevin & Mason, 2004; Davies et al., 2004). Regardless of many years of exploitation, through extensive mining and quarrying, there has been little work carried out on regional diagenetic trends and their relationship to the structural evolution.

This study builds upon previous work carried out within North Wales and Derbyshire (Al-Fadel, 1983; Walkden & Williams, 1991; Hollis & Walkden, 2002; Bevin & Mason, 2004; Mason & Malpas, 2006) and presents an updated sedimentological and palaeo-environment interpretation for the outcropping Asbian and lower Brigantian strata, with focus upon a detailed study on the Great Orme, Llandudno. Moreover, through detailed, multiscale outcrop and petrographical analysis, the diagenesis from an early marine-meteoric realm through to the burial realm is presented. This data has been supplemented by observation and data from Denbighshire and Flintshire, northeast Wales. The primary objective of this work is to ensure a robust description of the sedimentary architecture and
diagenesis in order to understand and predict the type, distribution, and composition of diagenetic processes and products.

5.2 Geological Background
The North Wales Platform was one of a series of carbonate platforms that developed in the Lower Carboniferous on stable footwall highs that formed during back-arc extension, north of the Variscan Orogen (Davies et al., 2004) (Figure 5.1, 5.2). During this period the UK was situated in an equatorial position giving rise to tropical seas and optimum conditions for the growth of carbonate platforms. The North Wales Platform, flanked by the East Irish Sea Basin to the north and St Georges Land to the south records the evolution of a ramp to rimmed shelf geometry from the Asbian to the Brigantian (Adams et al., 1990; Walkden, 1987) (Figure 5.3). The land-attached platform developed a steep, north to north-eastward facing margin, broadly in line with the present day coastline, which most likely comprised coral-algal build-ups in the Upper Dinantian (Bancroft et al., 1986). Close proximity to exposed land resulted in sporadic incursions of siliciclastic sediments throughout the Lower Carboniferous. Not much is known of the platform to basin transition. Carbonate sediment is thought to have been supplied to the basin as calciturbidites and debris flows (Davies et al., 2004 and references therein). In addition, mud dominated mounds have been recorded on the platform slope and within the basin (Bancroft et al., 1986; Davies et al., 2004).

Depositional environments within the Dinantian succession mainly comprise open marine or sheltered subtidal environments with high-frequency upward shallowing cycles overlain by exposure surfaces (Neaverson, 1935, 1937; Warren et al., 1984; Somerville & Strank, 1984a, b; Al-Fadel, 1985; Bancroft et al., 1986; Davies et al., 1989, 2004; Somerville et al., 1989). Similar time-equivalent cycles are observed on the Derbyshire and Askrigg Platforms (Walkden, 1987; Arthurton et al., 1988; Vanstone, 1998).

Carbonate sedimentation ceased during the Late Brigantian and gave way to clastic sedimentation predominantly sourced from the Wales-
Brabant Massif. Subsequently, within the basin, the black organic-rich Holywell Shales were deposited (Early Namurian, Pendleian to Yeadonian in age) (Davies et al., 2004). During the Late Namurian to Early Westphalian a secondary source of siliciclastic material was supplied in the form of turbidite-fronted fluvio-deltaic systems prograding southwards and westwards from the Pennine High to the northeast of the East Irish Sea Basin (Gawthorpe et al., 1988; Kelling & Collinson, 1992; Davies et al., 2004; Hallsworth & Chisholm, 2007). These deposits are known locally on the North Wales Platform as the Gwespyr Sandstones (Yeadonian to Langsettian in age) (Williams & Eaton, 1993; Jerrett & Sampson, 2007).

Sedimentation on the North Wales Platform was controlled by inherited Caledonian lineaments, which were then the focus for subsequent structural deformation. In particular, northeast-southwest, northwest-southeast and east-west faults were reactivated with a strike-slip component during the Variscan and Alpine Orogenies (Late Carboniferous and Tertiary respectively) (Morton, 1898; Smyth, 1925; Nicholls, 1968; Al-Fadel, 1985; Williams & Eaton, 1993). The strong fault control on sedimentation resulted in contrasting sediment thicknesses with Asbian successions reaching up to 800m in close proximity to large fault systems (Al-Fadel, 1983; Williams & Eaton, 1993; Leeder & Gawthorpe, 1987).

Studies from the eastern flank of the Clwydian Range (Al-Fadel, 1983) and adjacent highs (Derbyshire Platform and Askrigg Platform; Fraser et al. (1990)) suggest that burial of the Dinantian succession was to a depth of up to 2.5 km close to subsiding faults. However, the northern margin of the North Wales Platform remained a relative topographic high throughout the Carboniferous (Williams & Eaton, 1993) and burial depths did not reach more than 1 to 1.5 km (top Dinantian) (Al-Fadel, 1983). Surrounding basins (East Irish Sea and Cheshire) experienced burial depths of ~1 to 1.5km in the Carboniferous and maximum burial depths of ~4km (top Namurian) during the Cretaceous (Hardman et al., 1993; Floodpage et al., 2001) (Figure 5.4).
5.3 Study Area
This study provides an overview of six key outcrops (1. Great Orme; 2, Prestatyn; 3. Pentre Halkyn; 4. Trefor Rocks; 5 & 6. Meliden and adjacent outcrops) representing the exposed Asbian and Brigantian strata of the North Wales Platform (Figure 5.2, 5.5). The outcrops span an area of ~45km², full details can be found in British Geological Survey sheets 95, 107, 108 and 121 and corresponding memoirs (Smith, 1927; Warren et al., 1984; Davies et al., 2004). Focus in this paper is on the Great Orme, a headland situated on the North West coast of Wales, adjacent to the town of Llandudno. The Great Orme headland is 4km long by 0.8km wide and provides excellent exposure up to 200m thick of Asbian and Brigantian limestone that is locally dolomitised.

5.4 Techniques
The Asbian and Brigantian succession of the Great Orme and has been analysed through integrated field and petrographic description and correlation. Data has been recorded from natural outcrop and disused quarries using sedimentological logs that record over 350m of section from 14 localities, of which eight are on the Great Orme (Figure 5.5, 5.6; Appendix 1). The successions were systematically sampled to represent the full stratigraphy and range of facies. Where possible, samples were drilled as 1.5” diameter core plugs to avoid the effects of surface weathering. From these samples, 160 30µm thick polished sections were prepared and half stained with alizarin red S and Potassium ferricyanide following Dickson (1965). The polished sections chosen represent each facies within each formation (Fm.). These were then described petrographically using plane light techniques and cathodoluminescence (CL). Cathodoluminescence was achieved using a Cambridge CCL Cold Luminoscope 8200 mk3, operated at an accelerating voltage of 10Kv, a vacuum of 2 torr and a gun current of 300Kv. Photographs were taken using a Progres C10 Laser Optik System.
5.4.1 Major and trace element analysis

*In situ* Major and trace element analysis was carried out using electron microprobe and bulk analysis using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). The elements analysed included Fe, Mg, Mn, Ca, Sr, Al. Further quantitative analysis focused on elements likely to be associated with burial cements, such as Cu, Pb, Zn, Na and Rb.

ICP analysis was conducted using powdered samples of host rock limestone and individual cement zones. Powdered samples were treated with 6M HCl for 24 hours to digest the carbonate phases. Corresponding samples were drilled from hand specimens and their purity checked where necessary by XRD techniques. Trace element concentrations were measured using a Perkin-Elmer Optima 5300 dual view ICP-AES with reproducibility of 0.1‰ (1σ).

Electron microprobe analysis was carried out using 25µm thick, unstained polished sections, which were carbon coated prior to analysis. Trace element concentrations were measured using a Cameca SX 100 Electron Microprobe. Operating conditions: accelerating voltage of 15Kv, beam current of 20nA, beam size of 5 µm or 10µm and internal standards were used for calibration. (See also Appendix 8 to 13).

5.4.2 Stable isotope analysis

Stable isotope analysis was conducted at the University of Liverpool. Powdered samples of host rock and discrete cement phases were acquired using a tungsten-tipped dentist drill. Samples of calcite were reacted (to completion) with phosphoric acid under vacuum, at temperatures of 25°C (*sensu* McCrea, 1950). Gases were measured by dual-inlet, stable isotope ratio mass spectrometry using a VG SIRA10 mass spectrometer. Isotope ratios were corrected for \(^{17}\)O effects following the procedures of Craig (1957). Oxygen isotope data were adjusted for isotopic fractionation associated with the calcite-phosphoric acid reaction using a fractionation factor (\(\sigma\)) of 1.01025 (Friedman & O'Neil, 1977). Samples were run against an internal standard and all results were
reproducible to ±0.1‰ (2σ). All data is reported relative to the VPDB standard. (See also Appendix 10, 14).

### 5.5 Facies Distribution and Palaeoenvironments

The Asbian to Brigantian succession on the North Wales Platform comprises the Dyserth Limestone Group and the Gronant Group (Figure 5.6). Typically, these units consist of 5-10 metre successions of well bedded limestone that display shallowing upward facies capped by surfaces that show evidence for erosion, protosoil formation and subaerial volcanic activity (Al-Fadel, 1983; Walkden & Davies, 1983; Davies et al., 2004). Similar surfaces have been comprehensively described in other areas (Derbyshire, Anglesey, South Wales, Askrigg) by Walkden & Williams (1991), Wright (1992), Vanstone (1998) and general accounts by Davies et al. (2004). These exposure surfaces are often well developed above beds of skeletal and oolitic grainstone and are interpreted as cycle tops. Cycles within the Dinantian carbonates are based on the stacking patterns of observed transgressive and regressive facies, initially recognised within the North Wales successions by Ramsbottom and Somerville (Gray, 1981). Cycles within the regressive, Asbian successions are characterised by shoaling upward sedimentation, comprising thick bedded, pale grey or well bedded dark grey skeletal wacke-packstones, algal laminites and interbedded mudstones at the base. Cycle tops comprise skeletal, oolitic packstone-grainstones and stromatolitic build-ups and are overlain by irregular erosive surfaces/palaeosols. By comparison, Brigantian cycles display thinner, well-bedded argillaceous limestones, interbedded mudstones and are overlain by exposure surfaces (Ramsbottom, 1975; Somerville, 1977, 1979a; Gray, 1981). Comparative sedimentation patterns are evident on the Derbyshire and Askrigg Platforms (Power & Somerville, 1975; Ramsbottom, 1984).

On the Great Orme, the succession is divided into six lithostratigraphic units, the Pier Dolomite Fm., The Tollhouse Mudstone Fm., The Great Orme Fm., The Craig Rofft Sandstone Mb, The Bishops Quarry
Limestone Fm. and The Summit Limestone Fm. (Figures 5.6-5.12, Warren et al., 1984 and references therein). See below for further details.

**Pier Dolomite Formation (Asbian)**

The Pier Dolomite Fm. is located to the northwest of Llandudno, on the Great Orme and comprises dolomitised limestone. The Pier Dolomite Fm. is organised into 10cm to 50cm thick beds of skeletal (crinoid) packstones with alternating mudstone layers, 0.3cm to 0.5cm thick and infrequent mudstone beds of up to 40cm thick. Beds are bounded by dissolution enhanced planes and erosional contacts below mudstone units. There is evidence of weakly preserved unidirectional cross-bedding and in situ coral growth, but otherwise biogenic and sedimentary structures have largely been obscured.

Constituent allochems of initially high magnesium composition are well preserved and include abundant crinoid and coral debris of up to 3cm in diameter resulting in distinctive rudstone-floatstone beds. Matrix and minor allochems are no longer visible due to complete dolomitisation. The allochems are only poorly reworked. The majority of the units contain the same skeletal assemblage but size can vary (<1mm to 3cm). Exact initial porosity of the dolomitised limestone is unknown due to the extent of replacement, whereas current porosity is estimated at <10% and includes secondary fracture, vug and intercrystalline porosity.

The upward coarsening and cleaning trends of individual units (from mudstone to wackestone to pack/grainstone) suggests deposition under progressively higher energy conditions. The dominant biota, crinoid and echinoids are often associated with build-ups in shallow open marine environments (Flügel, 2004). In addition, in situ Syringopora ramulosa corals are ubiquitous, implying high levels of light penetration (op. Cit.). The generally high abundance of poorly-sorted, large, angular skeletal allochems indicates limited transportation whilst the clean texture implies sustained periods of high depositional energy, consistent with development of a high energy platform margin. It is suggested that the
environment of deposition is a platform shoal. The unidirectional cross-bedding point towards progradation of the shoal. Comparative deposits have been recorded by Bancroft et al. (1986) to the east of the Gloddaeth Syncline.

**Tollhouse Mudstone Formation (Asbian)**

The Tollhouse Mudstone Fm. overlies the Pier Dolomite Fm. on the Great Orme. The unit ranges in thickness from 1m to 4m and thins to the north-west. The contact with the underlying Pier Dolomite Fm. is not visible. The contact with the overlying Great Orme Limestone Fm. is gradational. The unit comprises reworked and un-micritised grains of crinoids, echinoid, dasyclad (green algae) and Productid brachiopods. The constituent facies are skeletal wacke-packstone with allochem size that ranges from sub millimetre to 2mm. Much of the sediment is dissected by solution seams and stylolites resulting in a nodular appearance on a sub-centimetre scale. There is no visible porosity and combined compaction and fine grained sediment any remaining porosity is micro-interparticle matrix porosity, estimated at <5%, as suggested by green colouration following blue resin impregnation.

Re-worked carbonate grains producing skeletal wackestone-packstones and the large quantity of mud present compared to the underlying Pier Dolomite Fm. suggests that deposition occurred in a lower energy environment with gentle winnowing. The diverse, normal marine fauna including an abundance of echinoderm fragments and green algae suggest the most likely environment of deposition is a relatively deep, protected subtidal environment on the platform top. This is supported by the presence of sharp walled burrows indicating soft but stable sediment. In addition, there are no indicators of deposition and/or flow on a high angle slope. Similar facies have been described for the subtidal sediments in the Llangollen area (Gray, 1981). The Tollhouse Mudstone Fm. has been correlated with the Dulas Limestone Fm. and porcelaneous
mudstone in Abergele by Warren et al. (1984), although these correlations remain an area of some debate (Bancroft et al., 1986).

Great Orme Limestone Formation (Asbian)
The Great Orme Limestone Fm. is the thickest formation on the headland (175m thick) comprising 20cm to 100cm thick beds. Bedding surfaces are generally planar and display dissolution enhancement. Individual beds typically comprise algal-laminated skeletal wackestones at the base of beds, coarsening into skeletal wackestones to crinoidal packstones and oolitic skeletal grainstones. Skeletal allochems are dominated by crinoid and echinoid fragments. Bed tops intermittently contain isolated corals and stromatolitic build-ups (20cm to 30cm thick). Erosion surfaces and the development of palaeosols are evident at the top of these coarsening and cleaning upward units. The limestone contains <1% secondary fracture porosity.

Beds regularly thin and coarsen upwards. This repetitive stacking pattern is interpreted as a series of coarsening upward successions, from a low energy, shallow water intertidal setting (algal laminites) into high energy subtidal shoal (oolitic skeletal packstone-grainstones). These deposits are capped by stromatolites established in very shallow water before exposure resulting in rubbly, red-stained palaeosols and/or karst.

Control on this cyclicity have been attributed to sea-level fluctuation and possible syn-depositional faulting (Gray, 1981; Warren et al., 1984), but may also be influenced by autocyclic processes within this high productivity setting characterised by shoaling and prograding successions.

Craig Rofft Sandstone Member (Asbian)
The Craig Rofft Sandstone Mb is situated towards the summit of the Great Orme. This member is 1m to 1.5m thick and weathers a distinctive pink colour. The unit grades upwards from grainstone to carbonate cemented sandstone and back to limestone again. The limestone above and below the sandstone are composed of skeletal, bioclastic and ooidal
grains. The quartz grains are well sorted, well rounded and medium-fine grained. Sedimentary and biogenic structures such as small scale northeasterly dipping cross-bedding, rootlet and/ or burrowing structures are observed within the outcrop. Craig Rofft is well cemented with less than an estimated <2% secondary fracture porosity and <1% solution enhanced vug porosity at the margins of dolomite crystals.

The northeast flow direction indicated by cross-bed sets would suggest that this sand incursion was most likely derived from ‘St Georges Land’ to the south. The medium-fine, well sorted and well rounded grains indicate mature sediment and a relatively long transport distance. The pink colouration is most likely the result of iron oxides. The evidence for biological activity suggests stable conditions in a shallow or marginal marine system. This is supported by the shallow high-energy limestone facies above and below with frequent development of palaeosols and minor karst surfaces. Similar facies changes have been noted within South Wales by Wright (1986) who concluded that they represent shore face deposits.

*Bishops Quarry Limestone Formation (Brigantian)*

The Bishops Quarry Limestone Fm. comprises dark grey, bioclastic wackestones and packstones with interbedded fissile mudstone. The well-bedded unit has bed thicknesses that range from 2cm to 50cm. Component allochems include a variety of reworked crinoids, echinoid, coral and brachiopod fragments. Towards the top of the formation brachiopod (*Gigantoproductid*) shells become more abundant and reach 20cm in size. The contacts between beds are sharp with evidence of compaction (flattened bioclasts and undulose surfaces). Small coral build-ups are evident at the top of beds and evidence of burrowing is seen in thin section. No visible porosity is observed although minor micro-interparticle matrix porosity is present as suggested by green colouration following blue resin impregnation.
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The fine grain size and muddy texture of the Bisho
ps Quarry Limestone Fm. suggests it was deposited within a relatively low energy environment allowing fine grained sediment to accumulate and provided conditions stable enough for brachiopod and other fauna and flora to thrive. The presence of in situ corals at the base of the formation indicates relatively shallow and clear water conditions whereas in situ brachiopod assemblages higher in the formation suggests either slightly deeper water or that light conditions had degraded (Flügel, 2004). The interbedded mudstones are composed of carbonate material most likely derived from the surrounding platform. The switch in sedimentation style is probably due to a slight deepening event temporarily halting coral growth. These deepening events appear to be frequent and short lived.

*Summit Limestone Formation (Brigantian)*

The Summit Limestone Fm. is located at the top of the Great Orme. The contact with the underlying Bishops Quarry Limestone Fm. is disconformable. The limestone is pale grey in appearance and rubbly. Beds are 20cm to 40cm thick with undulose bedding planes. The Summit Limestone Fm. is primarily composed of skeletal wackestone-packstone. Chert nodules are also visible parallel to bedding and along fractures. Component grains include sub-millimetre foraminifera and undifferentiated skeletal fragments. No visible porosity is observed although minor micro-interparticle matrix porosity is present as suggested by green colouration following blue resin impregnation.

The Summit Limestone Fm. is characteristic of a low energy, subtidal environment with prevailing fine grained sedimentation, limited winnowing and lack of bioturbation. Reworked Productid brachiopod fauna and skeletal allochems observed within the unit points towards normal marine assemblages. The Summit Limestone Fm. lacks interbedded mudstones, structure and cyclicity that may indicate supratidal or peritidal deposition and therefore a subtidal setting is interpreted.
The occurrence of chert has resulted from either the presence of siliceous organisms or an influence from interbedded mudstones and/or overlying siliclastic sediment as seen further east in Prestatyn. Full investigation of the chert was beyond the scope of this study and would require further petrographic and geochemical analysis to identify different phases, determine the diagenetic controls and place within the paragenetic framework outlined by this paper.

5.6 Paragenesis
Diagenetic features have been described from outcrop and petrographically. The relative timing of diagenetic events has been deduced from superposition and the cross-cutting relationships between the diagenetic features such as stylolites and fracturing. For full details of the diagenetic phases see Table 1 and Figures 5.9-5.13. (See also Appendix 4 and 7).

Micrite envelopes and crusts
Micrite envelopes and partial micritisation of grains are the earliest diagenetic features observed. They are prevalent across the North Wales Platform and form on skeletal and non-skeletal allochems. Micritisation of allochems is preferentially developed on foraminifera and shell fragments and varies in extent from minor envelopes (10µm thick) to complete replacement and loss of internal texture. CL displays dull brown to non-luminescent micrite and dull orange luminescence where neomorphism has occurred.

Grain fringing cements (M1)
The first cements to coat skeletal grains and undifferentiated allochems have fibrous to columnar, isopachous textures (Figure 5.12). They form crystals that are up to 500µm in length, inclusion poor and non-luminescent to dull orange luminescent. These cements are best developed on the platform margin within grainstone shoals, and become less common further onto the platform. Their distribution and non
luminescence, along with their isopachous texture is consistent with precipitation under moderate or high energy conditions from marine pore waters (Tucker & Wright, 1990). This is supported by the pre-compactional timing and lack of pendant morphologies, which would have implied precipitation under vadose conditions. Where these cements have a dull luminescence they have most likely undergone subsequent mineralogical stabilisation under reducing conditions, most likely during burial. Petrographically similar cements are documented on the Derbyshire and Askrigg Platform where they are more ubiquitous and well developed (Hollis & Walkden, 2012).

**Syntaxial and pore fill SC1-C4**

Syntaxial calcite cements SC1-SC3 and passive pore-filling C4 are volumetrically the most important cement phases on the North Wales Platform. The cements, best developed in grainstone facies, occlude the majority of all primary and dissolution enhanced porosity. SC1-SC3 are limpid, syntaxial cements that are most commonly associated with crinoid and echinoid grains that lack micrite envelopes. The overgrowths range in thickness from 50µm to 1000 µm. CL reveals non-luminescent calcite with bright yellow subzones (5 µm to 10µm thick) followed by very dull brown luminescent cement with subzones up to 30µm thick. C4 limpid, blocky crystals range in size from 50µm to 500µm. CL displays very dull brown to non-luminescent cement (Figure 5.12, Table 1). The cement zones are equivalent to zones 1 to 4 of Al- Fadel (1983).

SC1-SC3 and C4 cements post-date marine cements M1 and are cross-cut by stylolites and solution seams suggesting they pre-date compaction. In addition, they lack pendant or meniscus morphologies that would imply vadose conditions. The high frequency sub-zonation, blocky syntaxial nature and increasing crystal size of the cement is typical of meteoric-phreatic cement precipitated from a calcium carbonate saturated fluid into a fluid filled void (Walkden & Berry, 1984; Searl, 1988a,b, 1989; Flügel, 2004). The same textures have been recorded in the east of the study.
area (Al-Fadel, 1983) and on the South Lake District Platform (Horbury & Adams, 1989) and Derbyshire Platform (Walkden & Berry, 1984).

The non-luminescence, with high-frequency bright yellow subzones, exhibited by SC1-SC3 cements suggests precipitation from pore waters with fluctuating chemistries. Given the supporting petrographical evidence for precipitation from meteoric pore waters, the non-luminescence of these cements is consistent with precipitation from oxic pore waters. Bright luminescent subzones could reflect incorporation of Mn during periodic water table stagnation and lowering of Eh associated with sea level rise (cf Walkden & Berry, 1984; Horbury & Adams, 1989). The similarity in cement patterns at different stratigraphic levels is likely to result from water table fluctuations associated with multiple exposure events. In this context, dull luminescent cement C4 represents the earliest phase of burial cementation, perhaps from evolved meteoric pore waters (cf. Zone 3 of Walkden & Williams, 1991 and Zone Z3P of Hollis & Walkden, 2012).

Matrix replacive dolomite D0-D2
Matrix replacive dolomite is only evident on the northern margin of the North Wales Platform. The dolomite occurs as partially fabric retentive, turbid, xenotopic to euhedral interlocking mosaics, preferentially preserving crinoid and coral fragments (Figure 5.12). Crystal sizes range from 50µm to 1000µm and display homogenous red luminescence under CL (Table 1). Bed-parallel stylolites cross-cut phases D0-D2 indicating that they pre-date chemical compaction. The relationship between the D0-D2 dolomite phases and the early diagenetic phases are unclear; the fabric destructive texture means that it is not possible to determine if SC1-SC3 cementation predated dolomitisation. Nevertheless, evidence that dolomitisation predated stylolitisation suggests a relatively shallow burial depth, whilst the xenotopic fabric is suggestive of elevated fluid temperatures (perhaps >50°C; Sibley & Gregg, 1987).

Blocky fracture and secondary porosity fill C5 – C9
On the northern and eastern margin of the North Wales Platform calcite cements C5 – C9 were observed in matrix pore systems and fractures. Their characteristics are described in Table 1 and below. The orientation of joint planes and calcite-cemented fractures display dominant north-south and northeast-southwest orientations. Phases C5-C9 occur as limpid fracture fill cements with blocky and drusy textures. Crystal sizes range from 20µm to 200µm. CL reveals bright orange and dull orange zoned calcite. The bright orange phase C5 is intergrown with fluorite, galena and chalcopyrite (Figure 5.11).

Stable isotope analysis of C5-C7 measured $\delta^{18}$O$_{\text{calcite}} = -8.31$ from to -6.55 ‰ VPDB and $\delta^{13}$C = 0.23 to 2.17 ‰ VPDB. The distribution of Zones C5-9 in fractures, and their bright – dull luminescence along with their intergrowth with fluorite, galena and chalcopyrite is suggestive of precipitation in the burial diagenetic realm, from anoxic, metal-enriched brines. The relatively light $\delta^{18}$O values could indicate fractionation with increasing temperature during burial and/ or the influence of fluids depleted in $\delta^{18}$O, whereas the carbon isotopic signature remains close to the values for lower Carboniferous marine pore waters.

*Stylolitisation and compaction*

Stylolites are observed across the North Wales Platform. They occur primarily within finer grained lithologies and at bed boundaries. The stylolites are mostly orientated parallel to bedding although stylolites parallel to fractures have been recorded. They vary from low amplitude solution seams to moderate amplitude sutures (<0.2mm to 2cm in height) with well developed fractures and contain insoluble material. In addition, many stylolites appear to have been opened and host calcite cements and metal mineralisation.

*Calcite cements C9b-C11*

Confined to fault zones (local limestone matrix replacement), fractures, stylolites and secondary dissolution porosity, C9b-C11 crystals are predominantly blocky, form interlocking mosaics and display ferroan
staining (Table 1). Crystal sizes range from 10µm to 200µm. CL reveals alternating bright and dull luminescent subzones and a subsequent dull orange-brown cement. Cement C9b post-dates dissolution, as revealed by the etched margins of host porosity. Their distribution within fractures and along stylolites implies precipitation in the deep burial realm, and their bright-dull luminescence is consistent with this, with incorporation of Mn (and Fe) under reducing conditions. Subsequent dull cement is either a result of increased iron and/or depletion in Mn, further trace element analysis would be required to confirm this.

**Vein dolomite D3-D7**

Five phases of fracture related dolomitisation have been identified from the Great Orme on the North Wales Platform margin (D3-D7). D3-D4 cements display xenotopic to euhedral textures comprising rhombic dolomite with curved crystal faces and an increase in iron-oxide inclusions toward the crystals margins. These phases are mainly restricted to fractures, cross-cut compaction features such as stylolites and progressively replace earlier dolomite phases (Figure 5.11). D3 dolomite has a homogeneous, dull red luminescence, whereas D4-D5 displays some zonation and etched crystal margins. Phases D6 to D7 are restricted to fractures, display dark red to bright pink luminescence and etched margins. A complete description of these phases is beyond the scope of this paper (see Juerges et al., in prep; Chapter 6 and 7), but their geochemical and petrographical properties are described in Table 1 and 2. Overall, the xenotopic and saddle morphology of D3-D7, along with their distribution within fractures and along stylolites is consistent with precipitation at elevated temperatures (>60°C; Radke & Mathis, 1982; Sibley & Gregg, 1987) in the burial environment.

**Vug and micro-fracture fill C12-C14**

Phases C12 to C14 have been recorded primarily from the northern platform margin. The cements are limpid, blocky to rhombic with etched margins. Crystals range in size from 100µm to 700µm. CL displays dull
brown to bright orange-yellow outer zones, concentric subzones of very dull brown and non-luminescent cement with infrequent bright yellow to pinkish subzones. Subzones are 5µm to 30µm thick with variable frequency. The lack of luminescence and concentric subzonation has led to a tentative meteoric cement interpretation. This is also supported by the subsequent etching which suggests further disequilibrium between pore fluids and the carbonate cements.

**Rhombic calcite C15**

C15 vein calcite has only been recorded from the Tollhouse Mudstone Fm. on the Great Orme. It occurs within north-south striking fractures that host earlier dolomite cement and exhibit evidence of reactivation through crack-seal vein textures. The calcite appears rhombic and turbid in plane light, similar to D2, whereas CL reveals a homogenous bright yellow luminescence. Crystal sizes range from 200µm to 500µm. Stable isotope analysis indicates $\delta^{18}O = -2.25$ to $-1.68 \, \%$ VPDB and $\delta^{13}C = -12.70$ to 12.43 $\, \%$ VPDB. The bright luminescence implies precipitation from anoxic fluids, whilst $\delta^{13}C$ data suggests a source of isotopically light carbon such as organic material or meteoric fluids. Concentrations of Mn (1820-8940 ppm) and Fe (3100 – 120860 ppm) agree with a reducing environment. However, the higher Fe concentration and also the variable but large Mn/Fe ratios (1:20) are contradictory to the bright luminescence.

**Secondary pore-filling cement C16-C19**

Phases C16 to C19 occur within secondary, dissolution enhanced vugs within all formations on the Great Orme, northern platform margin. Crystals are blocky and limpid. Crystal sizes range from 20µm to 100µm. CL reveals alternating non-luminescent and bright yellow luminescent subzones of variable thickness (5 - 50µm) and frequency. Petrographic characteristics are similar to those of the syntaxial SC1 and SC2 cements but cross-cut early diagenetic and burial phases (e.g. D1-D2, Figure 5.12, 11). Trace element maps suggest the high frequency alternations in
luminescence are controlled by minor variations in Mn as Fe is uniformly low within the calcite.

**Laminated fracture fill**
Infrequent open-mode fractures observed on the northern margin of the platform contain alternating laminated layers and fringing calcite cements, with small spherical calcite nodules. The fractures are 0.05cm to 0.5cm thick and cross-cut all previous diagenetic phases. It is not uncommon for these fractures to display secondary porosity, formed by dissolution, as evidenced by truncation of the cement.

**Dissolution enhanced fracture and vug porosity**
The final diagenetic phases viewed on the North Wales Platform are open fractures and vug porosity. Fractures 0.5cm to 1cm wide are seen throughout the platform but are more prevalent along the platform margin. The secondary, dissolution enhanced porosity appears to be preferentially developed at the margins of replacive dolomite whilst vugs of up to 20cm diameter occur throughout the dolomitised facies and display uneven and scalloped edges.

**5.7 Distribution of Mineralisation and Hydrocarbon**
Mineralisation on the North Wales Platform is predominantly fracture-hosted, within limestone and dolomite. Fractures range in size from sub-millimetre to metre scale and display a range of blocky and drusy textures often indicating passive fill. Minerals include galena, sphalerite, fluorite and barite, which are mainly restricted to fractures, secondary dissolution porosity and proximal to re-opened stylolites. The principal gangue mineral is calcite. The economic mineral assemblage decreases in volume away from the north-east and eastern platform margin, with only minor amounts recorded to the northwest on the Great Orme (Lewis, 1996).
Copper-iron minerals (principally chalcopyrite) are restricted to the northern platform margin (Great Orme, Meliden and Prestatyn). The
mineralisation occurs mainly within north-south trending joints and is coeval with late calcite cementation (C15). Lewis (1996) and references therein have suggested that copper mineralisation is spatially and temporally related to dolomitisation. However, field and petrographic observations from this study demonstrate that the mineralisation post-dates the last dolomitisation event (Figure 5.11).

Minor volumes of hydrocarbon (bitumen) have been observed on the North Wales Platform on the Great Orme and around Halkyn, within this study and documented in the literature (e.g. Parnell, 1983a, 1992; Parnell & Swainbank, 1990). However, no hydrocarbon inclusions have been observed during the course of this study.

5.8 Discussion and Interpretation

This study focuses upon the sedimentology and diagenesis of a Lower Carboniferous, Dinantian platform margin succession. The stratigraphy has been broadly outlined by Warren et al. (1984) and Hind & Stobbs (1906). For the purposes of this study, more detailed description of lithofacies than has previously been published has aided the interpretation of the diagenetic history by providing the framework in which the initial distribution of porosity can be described. The results of the subsequent diagenetic evaluation illustrate a complex diagenetic history for the North Wales Platform and in particular the Great Orme. Five diagenetic environments have been interpreted including marine, meteoric, shallow burial, deep burial and telogenetic. Several phases of cementation from early marine-meteoric through multiple generations of dolomite and subsequent secondary pore-filling calcite record the successive overprinting and reduction in porosity (Figures 5.12-5.15).

*Diagenetic environments*

*Depositional framework*
During the course of this study five depositional environments have been defined; emergent, restricted lagoon, shallow subtidal, deep subtidal and platform margin (Figure 5.15). These interpretations are consistent with and enhance previous studies, for full details see (Gray, 1981; Warren et al., 1984; Somerville et al., 1984, 1989) and lateral equivalents (Gray, 1981; Al-Fadel, 1983; Davies et al., 2004). The sedimentological data presented within this study indicate a range of shallow-marine shoaling and subtidal facies that are characteristic of platform top and margin environments (Figure 5.12, 5.14, 5.15). The Pier Dolomite Fm. comprises dolomitised, shallow water, crinoidal shoal limestone and minor interbedded mudstone. These are overlain by the Tollhouse Mudstone Fm. composed of skeletal mudstone-packstone and represent a sheltered subtidal environment. Laterally equivalent units on the Little Orme and Abergele include the porcelaneous Dulas Mudstone and reef facies (Warren et al., 1984), highlighting the differences in energy and laterally variable facies of these contemporaneous depositional environments.

The Great Orme Limestone Fm. is comprised of upward shallowing, transgressive-regressive cyclical limestone units capped by exposure surfaces and/or palaeosols (Figure 5.14). The formation displays wacke-grainstones facies typical of subtidal to peritidal environments. Cycles at the base of the Great Orme Limestone Fm. are bound at the top and base by algal facies typical of very shallow intertidal/peritidal environments whereas the top of the formation display cycles that lack evidence of algal lamina. Comparatively, red palaeosols become more frequent and more developed towards the top of the formation. These observations are consistent with the overall regressive nature of the Asbian succession (Warren et al., 1984). Cyclicity was potentially controlled by autocyclic, tectonic and eustatic processes (e.g. Gawthorpe, 1987), the details of which are beyond the scope of this study.

No large reef build-ups have been recorded within the outcropping succession on the Great Orme although, the adjacent Little Orme and Nant-y-Gamar host reef and bryozoan build-ups (Warren et al., 1984; Bancroft et al., 1986). This could suggest that the platform margin was
characterised by discontinuous patch reefs, knolls and shoals and is consistent with the subtidal mud and wackestones interfingered with coarse high energy facies. The shoals and patch reefs could have provided shelter from wave action and enabled fine grained sediment with normal marine assemblages to accumulate (e.g. Ronchi et al., 2010).

Towards the end of the Asbian small pulses of siliclastic sediment were deposited (Warren et al., 1984) in more distal platform areas. On the Great Orme, this pulsing of siliciclastic sediment is represented by the Craig Rofft Sandstone Member. The sediments were most likely sourced from the Wales-Brabant Massif to the south and south-west. Siliciclastic deposits have also been observed on Anglesey to the west of the Great Orme, an area considered more proximal to the palaeo-coast (Walkden & Davies, 1983). The increase in siliclastic deposition is likely to have coincided with the onset of Variscan uplift associated fall in relative sea level (Gawthorpe et al., 1988; Kelling & Collinson, 1992; Davies et al., 2004; Hallsworth & Chisholm, 2007).

Brigantian sedimentation occurred following a marine transgression across northern England and Wales (Warren et al., 1984). On the Great Orme cyclical wackestones to packstones of the Bishops Quarry Limestone Fm. were deposited and the partially dolomitised, chert rich mudstones-packstones of the Summit Limestone Fm. The stacking pattern and faunal assemblages of the Bishops Quarry Limestone Fm. are comparable to those observed in Llangollen (e.g. Gray, 1981) and record frequent drowning of shallow marine fauna. The Summit Limestone Fm. has previously been interpreted as representing basinal deposition. However, considering the absence of evidence for platform slope structure and evidence of a major eustatic rise elsewhere on the platform it’s not unreasonable to consider the formation representative of a subtidal, platform top environment and the development of a turbid water column due to the influx of siliciclastics. This may have implications for the interpretation of laterally equivalent formations to the east, around Prestatyn (e.g. Somerville et al., 1989).
Timing and controls on fluid flow and cementation

Early diagenesis

Early diagenesis embraces all diagenetic events (cementation, fracturing and dolomitisation) that take place before significant burial (<300m burial, prior to the onset of stylolitisation) and include the marine and meteoric realms (Figure 5.12).

Marine diagenesis is characterised by isopachous grain fringing cements (M1) and micritisation. M1 locally precipitated in cleaner facies on the higher energy platform margin. Preservation of these delicate cement morphologies was most likely a result of early, rapid precipitation of the subsequent pore-occluding blocky calcite prior to compaction.

In outcrop there is clear evidence of extensive meteoric diagenesis through the development of calcretes, karst and palaeosols at the top of upward-shallowing units, indicating several prolonged periods of exposure. Similar observations have been documented from high frequency cyclic deposits on adjacent platforms (South Wales: Raven, 1983, 1984; Wright, 1992; Searl, 1988. Derbyshire: Walkden & Williams, 1984; Horbury & Adams, 1989. Alston/Askrigg: Tucker, 2003; Gawthorpe, 1986). There is clearly strong evidence for frequent changes in relative sea level, although the interplay of glacio-eustacy, tectonism and autocyclic processes remains an area of some debate.

Meteoric diagenesis across the North Wales Platform is characterised by syntaxial overgrowths of non-ferroan calcite, preferentially seeded on crinoid and echinoid fragments and interparticular pore-filling cement characterised by cement phases SC1-SC3. These cements are interpreted to be equivalent to calcite zones 1-3 observed in Llangollen (e.g. Solomon, 1989). Such cements are common within periods of calcite rich seas (Walkden & Berry, 1984) and are also described from the Derbyshire Platform (Walkden & Williams, 1991), the South Lakeland High (Horbury & Adams, 1989), and the Askrigg Platform (Hollis & Walkden, 2012). The presence of multiple palaeokarst surfaces across the North Wales Platform suggest that meteoric conditions were frequently established during sea-level lowstands and recharged by St
Georges Land to the south. The periods of emergence range between a few thousand to a few tens of thousands of years (Walkden, 1974, 1983; Wright, 1982; Walkden & Williams, 1987) providing enough time for, meteoric phreatic lenses to develop (Chilton, 1992). The occlusion of primary and secondary porosity, the lack of vadose cement textures and/or dissolution prior to cementation suggests the pores were completely filled with calcium carbonate saturated fluids typical of a meteoric phreatic environment.

Dolomite cement phases D0 to D2 were described only from the northern platform margin, preferentially replacing precursor high-Mg allochems such as crinoid ossicles and echinoid fragments. These skeletal allochems were the dominant constituents of coarse grained skeletal pack/grainstone beds within the Pier Dolomite Formation. Crinoids and echinoid fragments are single crystals and are therefore common nucleation sites for calcite (Walkden, 1984; Walkden & Berry, 1984; Flügel, 2004), and in this case also for dolomitisation. Mimetic replacement is favoured by super saturation with respect to dolomite and the presence of magnesium (Sibley, 1991) suggesting the high abundance of high magnesium rich allochems, the circulation of Mg-enriched fluids along high permeability beds and/or thermochemical conditions suitable for dolomitisation initiated dolomitisation. The controls on dolomitisation in the Pier Dolomite Formation are explored in more detail in Juerges et al. (in prep) and Chapters 6 and 7. What should be emphasised here is the strongly stratabound geometry of D0-D2 dolomite, which is concentrated in the Lower Asbian, and which terminates beneath the Tollhouse Mudstone Formation, providing good evidence that fluid circulation higher in the succession was inhibited by the presence of low permeability beds. In addition, cross-cutting relationships with stylolites indicate pre-compactional dolomitisation, and although the relationship to SC1-4 remains ambiguous, dolomitisation most likely occurred during early burial.

Burial
Subsidence of the Dinantian succession of the North Wales Platform took place during post-rift subsidence of the Pennine and East Irish Sea Basins, with infill of topographic relief and burial beneath the siliciclastic sediment pile. Following occlusion of the primary porosity, faults and fractures became the primary conduits that enabled fluid migration. Cement phases C5 to C9 occur as blocky, ferroan calcite, cross-cut stylolites and are cross-cut by D3-D7 saddle dolomite, which characterise the fracture-fill burial cements and suggest fluid temperatures of >60°C. Cement C5 is intergrown with fluorite, galena and chalcopyrite, indicating that a flux of mineralising fluids was circulating on the North Wales Platform at this time. Stable isotope values are variable and indicate only minor fractionation and/or influence from δ¹⁸O depleted fluids. δ¹³C values mostly fall within the range of normal marine values for Late Dinantian sea water (-2‰ to +4‰ VPDB), based on the analyses of pristine brachiopod shells and marine calcite cements (Popp et al., 1986; Veizer et al., 1997). The marine carbon signature reflects a marine origin for the formational brines with minor buffering by the host-rock limestone. Late dolomite phases with distinctly lower than estimated marine values suggest a basinal fluid source that have interacted with organic material and late de-dolomite suggest influence from meteoric fluids. The start of the mineralisation across the North Wales Platform suggests circulation of hot formational brines most likely from the basin. However, localised dolomite cementation on the Great Orme, Little Orme and Prestatyn may indicate preferential activation of some faults and/or access to a different basinal fluid source. Rapid deposition of Late Dinantian and Namurian basin sediments within the EISB and to a lesser extent in the proto-Cheshire Basin (Smith, 1999) could have retained basin fluids and limited the flux during burial. This would be consistent with fluid flux and retention suggested for the adjacent age equivalent Askrigg and Derbyshire Platforms (Hollis & Walkden, 2012). Moreover, burial of the EISB and Cheshire Basin during Late Carboniferous occurred to depths of ~1km (top Namurian) and minor hydrocarbon production (Hardman, 1993; Floodpage, 1997) would have provided the
potential for trace element and metal transport. However, the limited burial depths and hydrocarbon production is likely to have limited the release of trace elements and their means of transport resulting in limited MVT mineralisation during the Variscan compression. Elsewhere on the North Wales Platform pulsed fluid expulsion from the basin lead to more mineralisation, and most likely driven by faulting/fracturing associated with the Variscan Orogeny.

**Variscan Inversion**

Uplift, exposure and erosion related to the Variscan tectonics took place during the Late Carboniferous. This inversion event would have most likely renewed meteoric conditions. It is difficult to assess the impact the Variscan Orogeny had on peripheral areas such as North Wales due to the nature of the outcrops and lack of preserved post-Carboniferous sediment. However, late vein fill calcite has been observed (C12) following D6-D7 and C8-C11. C12 contains very low Fe, Mg and Sr concentrations. Mn is also low, although zonation with slightly elevated concentrations can be seen on the trace elements maps (Appendix 9). The elevated Mn is most likely controlling the fine concentric bright zonation within largely non-luminescent crystal as revealed by CL analysis. The concentric zonation is consistent with the description for meteoric cement (e.g. Walkden & Berry, 1984).

**Re-burial**

Regional tectonic extension prevailed across northern England and Wales from the Permo-Triassic until the Late Cretaceous- Early Tertiary and the onset of Alpine compression. This reactivated faults with an east-west orientation, resulting in fault/ fracture related fluid migration through the North Wales Platform and deposition of C13 - C16 and copper mineralisation at the platform margin. The fractures cross-cut N-S orientated structures and the cements that are potentially related to Variscan uplift, therefore they are interpreted as Mesozoic in timing. The copper mineralisation can be seen to exploit secondary porosity and
fractures that cross-cut dolomitisation at the platform margin. The source of the copper rich fluids is still poorly defined. Possible fluid sources include Permo-Triassic basinal fluids, downward migrating marine, meteoric and/or formational fluids derived from the overlying successions or from the Lower Palaeozoic (volcanic and metasediments) basement to the south. Fluid derived from the Permo-Triassic sediment is considered to be the most probable as Variscan compression and related basin dewatering would have depleted the Late Carboniferous basin sediment of metal rich fluids. Further isotopic and geochemical analysis is required to fully constrain this.

Permo-Triassic and Jurassic extension could have potentially introduced downward migrating interstitial fluids into the Dinantian host limestone, from the overlying siliclastic sequences, within reactivated structures and following topographic head. During fluid migration through Permo-Triassic and Jurassic sediment elements (Pb, Zn, Cu) would have been leached and transported down into the Dinantian succession via the fault and fracture networks. This is consistent with observations of late copper mineralisation exploiting reactivated fractures and secondary porosity. This is also consistent with the location and fluid source for other copper deposits in northern England Alderley Edge where mineralisation is hosted by major faults and adjacent permeable horizons within the host-rock (Holmes et al., 1983) (see also chapter 6).

Maximum burial within the EISB and Cheshire Basins was achieved during the Jurassic and resulted in hydrocarbon production and increased potential for widespread release and transport of trace elements. The North Wales Platform was also reburied to depths of ~1km (top Dinantian) (Al-Fadel, 1983). Trace elements (Mg, Fe, Mn) could have been sourced from the dissolution of clays and detrital silicates during diagenesis (Jackson & Beales, 1967; Coleman et al., 1989b; Neilson & Oxtoby, 2008). Moreover, evaporites within the post-Carboniferous succession (Arthurton, 1980; Jackson et al., 1997) could have produced saline interstitial fluids capable of dissolving and transporting the metals and
trace elements (Sverjensky, 1981). The copper precipitated out of solution as a sulphide most likely within a reducing environment suggesting the presence of hydrocarbon, hydrogen sulphide and/or existing sulphides (e.g. pyrite, galena, and sphalerite) (Plant & Jones, 1989). Localised hydrocarbon (bitumen) is observed on the North Wales Platform although the volumes are negligible (Parnell, 1988; Eakin & Gize, 1992; Bevins, 1994) limiting the control on mineralisation. Cross-cutting relationships with earlier fault/ fracture hosted Pb-Zn sulphides has been observed across the North Wales Platform margin and also reactivation of these faults which could have provided the conditions necessary for precipitation.

**Telogenesis**
Calcite phases C16 to C19 are non-luminescent with bright yellow-pink concentric subzones. They are present as blocky and rhombic crystals that occur within secondary dissolution enhanced vug porosity that cross-cut all other phases and specifically post-dates Cu mineralisation. Petrographic characteristics are not dissimilar to SC1-SC2. They have been interpreted as meteoric cements following exposure the North Wales Platform during uplift. This is also supported by the presence of dedolomitisation, a common occurrence in the telogenetic realm (Choquette & Pray, 1970; Flügel, 2004). Should meteoric digenesis have occurred during Variscan uplift, it is likely that the subsequent burial (Jurassic) and Tertiary uplift would have overprinted this diagenetic stage. It is therefore more probable that the final meteoric phases are related to exposure following the second uplift event in the Tertiary.

**5.9 Comparison of the diagenesis with the Derbyshire and Askrigg Platforms**
Many similarities exist between the early diagenesis of the North Wales, Derbyshire and Askrigg Platforms. However, differences in paragenesis and cement characteristics become more apparent during burial.
Similar depositional environments were established during growth of the North Wales, Derbyshire, Askrigg and South Lakeland Platforms giving rise to comparable early diagenetic products. Early marine cements present as fibrous turbid/ limpid calcite precipitating around allochems (Hollis & Walkden, 2012). Subsequent primary and dissolution enhanced pore-occluding calcite cements (SC1-SC3 in North Wales (Solomon, 1989; this study), AZ1-3 in Derbyshire Hollis, 1996 and Zone 1-3 on the Askrigg Platform Walkden & Berry, 1984) occur as syntaxial overgrowths. The syntaxial cements are non-luminescent to dull brown luminescent, contain concentric zonation and staining that indicates non-ferroan calcite (Hollis & Walkden, 2012).

When comparing the burial diagenesis between the adjacent platforms greater differences are present. The North Wales and Derbyshire Platforms host fault/ fracture related dolomite. Dolomite on the Askrigg Platform does not form a fault/ fracture body and is potentially related to early release of fluids from the basin. In contrast to the Derbyshire and Askrigg Platforms, the North Wales Platform hosts a complex paragenetic history with 19 calcite and 7 dolomite cement phases. Paragenetic complexity on the North Wales Platform appears to increase towards the platform margin and close to deep-seated lineaments where fracturing and faulting at a local scale is more pronounced. Minerals such as fluorite, barite and galena are intergrown with the later burial calcite cements however, in contrast to the Derbyshire and Askrigg Platforms the volume of mineralisation and in particular fluorite and barite is much lower.

- Fluid Source and flow pathways; Field and petrographic evidence suggests fracture controlled, burial fluid-flux was orientated north-south on the North Wales Platform (this study) and roughly east-west on the Derbyshire Platform (Hollis & Walkden, 2002), exploiting deep seated lineaments and reactivated fault/ fracture systems. This is consistent with south-southeast-north-northwest compression related to the Variscan Orogeny. During the Variscan
compression mineralising fluids would have originated from the East Irish Sea Basin and to lesser degree Cheshire Basin, whereas, the burial fluids for the Derbyshire Platform originated from the Edale, Widmerpool and Staffordshire Basins (Hollis & Walkden, 2002). The Namurian shales and diagenetic fluids from the basins are thought to be the source and means of transport for the trace elements responsible for the platform hosted mineralisation (Pb-Zn). This comparable source is supported by the distribution (decreasing away from the platform margins) of MVT or Pennine style mineralisation across both platforms. However, variations in geochemical composition between basins are likely to occur, if only minor. This could affect the type of and volume of mineralisation present on the platforms.

- Post-Carboniferous clastic successions are postulated as the trace element source for late copper mineralisation on the northern North Wales Platform margin. Similar occurrences are observed on the margins of the Derbyshire Platform and within several Permo-Triassic basins around the UK. This close relation to the Permo-Triassic red beds and exploitation of reactivated faults/fracture networks, that dissect syn and post Carboniferous successions, points towards a common siliclastic source (Holmes et al., 1983). In addition, the presence and orientation of permeable structures potentially controlled the non-uniform distribution of mineralisation on the North Wales Platform allowing fluids to be driven on to the platform.

- Burial history; Basins surrounding the North Wales Platform experienced two burial episodes; during the Late Carboniferous (burial depth of ~1km, top Namurian) and reaching a maximum burial of ~4km in the Late Cretaceous-Early Tertiary (Hardman et al., 1993; Floodpage et al., 2001). Geothermal gradients of 30°C km⁻¹ have been invoked by Al-Fadel (1983) and Hardman et al. (1993). This implies that temperatures of the Namurian basin
shales reached between 30°C and 60°C during the Late Carboniferous and hydrocarbon maturation (Hardman et al. 1993) and trace element release most likely occurred immediately prior to Variscan uplift. Widespread hydrocarbon generation and migration occurred in the Late Cretaceous (Hardman et al., 1993) suggesting the trace elements responsible for the mineralisation were more widely available during maximum burial. In addition, overlying, post-Carboniferous siliciclastic sediments could have provided a change of trace element composition during this second phase of burial and subsequent uplift. This is consistent with observed, later copper mineralisation. By comparison, the basins surrounding the Derbyshire Platform experienced one episode of burial, maximum depths of 3km and temperatures over 90°C during the Late Carboniferous (Hollis, 1998). Moreover, hydrocarbon generation and migrations occurred on the Derbyshire Platform providing a means of trace element and metal transport (Hollis, 1996, 1998). These differences in burial history and therefore timing of trace element release and means of transport (organic complexes) are likely to contribute to the lower volumes of Variscan MVT mineralisation on the North Wales Platform and variation in type of mineralisation with time.

5.10 Conclusions

Focusing on outcropping Lower Carboniferous strata of the Great Orme, this study documents the sedimentology and diagenetic events for the North Wales carbonate platform. Field study and petrographical analysis have enabled the following conclusions to be made:

The nature of the outcropping Dinantian strata and the focus of study towards ramp to shallow marine platform units also highlights the limited knowledge there is regarding sedimentation and processes at the North Wales Platform margin.
Early diagenesis is recorded as marine and meteoric cements. These cements are found to occlude all primary porosity. Early cementation has predominantly been preserved within the grainstone units found at the centre and towards the top of shoaling upward cycles. The cementation took place within regressive units during frequent sea-level fall and exposure. These cycles are often topped by minor dissolution surfaces and/or the development red calcretes.

Late diagenetic cements are predominantly confined to the faults and fractures. Secondary porosity development can be observed in close proximity to the through-going fractures and along bedding planes. The secondary porosity is partially occluded by diagenetically late meteoric calcite that post date the main stage of burial and burial cement phases, thus indicating a telogenetic environment.

Matrix replacive and vein dolomite phases (D0-D7) are recorded on the platform margin. The dolomitisation most likely represent two main fluid flow events.

In total nineteen calcite cement phases have been defined by petrographic and CL analysis, which document the progressive burial and exhumation of the Great Orme succession, North Wales. The fluids responsible include marine pore waters, meteoric fluid from aquifers that became established during the waning extension in the Lower Carboniferous. With continued burial, fluids became modified. MVT mineralisation and late burial cements precipitated as a result of basin de-watering during the Variscan Orogeny. Subsequent copper mineralisation occurred during the Late Palaeozoic potentially related to Early Tertiary, Alpine uplift.

When compared to other Lower Carboniferous platforms within the adjacent Pennine Basin, the North Wales platform displays a more complex paragenesis. Similar galena, sphalerite, copper and dolomite
mineralisation is observed on the margins of the Derbyshire Platform. However, the North Wales Platform lacks the volume of minerals such as fluorite found in abundance on the Derbyshire and Askrigg Platforms. This is most likely due to a difference in basinal fluid source, host-rock composition and timing of trace element release.

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**Figures**

Fig.5.1. Palaeogeography of the UK including NE Wales - East Irish Sea area and Derbyshire, for the Early Carboniferous (Asbian-Brigantian) (modified from Fraser & Gawthorpe, 1990; Davies et al., 2004). ISB: Irish Sea Basin, CB: Craven Basin, SWS: South Wales Shelf, NWS: North

Fig. 5.3. Schematic N-S section for the North Wales displaying the change in sedimentation style from ramp to rimmed platform during the Lower Carboniferous (Somerville et al., 1989).
Fig. 5.4. Burial history curves for (a) the East Irish Sea Basin (Floodpage et al. 1997) and (b) the North Wales Platform (Al-Fadel 1983).
Fig. 5.5. Location map displaying the sampling positions and the locations of sedimentary logs, North Wales Platform, UK. Be: Berw Fault, D: Dinorwic Fault, AD: Aberdine Fault, CV: Clwyd Valley Fault (modified from Warren et al., 1984.)
Fig. 5.6. Composite stratigraphic diagram for NE Wales, Lower Carboniferous (Asbian - Brigantian) (modified from Warren et al., 1984; Davies et al., 2004; Waters & Davies, 2006). Red boxes indicate key outcrops from this study.

Fig. 5.7. Schematic palaeogeography across North Wales and stratigraphic log for the Great Orme (modified from Waters and Davies, 2006). Red dot: Great Orme.
Fig. 5.8. Picture of the Great Orme with the main sedimentary cycle boundaries depicted by black lines and a schematic composite log, (locations in Fig. 5.5). Not to scale. Green line indicates one log transect.
Fig. 5.9. Summary photopanel of the main facies types observed on the Great Orme (A) Interlocking matrix replacive and fracture hosted dolomite, Pier Dolomite Formation, C = crinoid fragment, D1-D3 = interpreted dolomite phases; (B) Skeletal packstone Tollhouse Mudstone Formation,
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Cp=chalcopyrite; (C) and (D) packstone-grainstones, Great Orme Limestone Formation; (E) Bioclastic grainstone, top of Great Orme Limestone Formation, O = ooid, FC = fringing cement; (F) Medium grained sandstone with calcite and dolomite intergranular cement, Craig Rofft Sandstone Member, taken with crossed-polars (G) Skeletal wackestone- packstone with burrows -B, Bishops Quarry Formation, taken with crossed-polars; (H) Mudstone with fractures, Summit Limestone Formation, taken with crossed-polars
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dolomite, Pier Dolomite Formation; (F) Fabric retentive, matrix replacive
D0-D, Pier Dolomite Formation, x4
Fig. 5.11. Photomicrograph of the late diagenetic features, cements and mineralisation (A) Chalcopyrite within a calcite cemented fractured hosted by dolomitised limestone, Pier Dolomite Formation, C = calcite, Cp =
chalcopryite; (B) Late meteoric calcite in secondary dolomite porosity, 
MC= meteoric calcite, D1-D2= interpreted dolomite phases, CL; (C) and 
(D) M= mineralisation (chalcopryite and quartz) , C= clays, Plane light and 
corresponding CL image, Great Orme Limestone Formation; (E) and (F) 
BC= Burial calcite, D6= late fracture controlled dolomite, Great Orme 
Limestone Formation strike slip fault, Plane light and corresponding CL 
image ; (G) and (H) MC= meteoric cement with vadose textures. Plane 
light and corresponding crossed-polars image, Great Orme Limestone 
Formation
Fig. 5.12. Photomicrograph of post-dolomite, late burial and telogenetic meteoric cements (A) vein fill, late burial calcite cement (B) multiple vein fill, late burial calcite cement with zonation, CL; (C) late porosity calcites, late post-burial meteoric cement, CL (D) meteoric calcite; (E) and (F)
Late non-luminescent cementing and replacing the margins of saddle dolomite, DD: De-dolomite, C: calcite, in plane light and CL respectively; (G) (H) De-dolomitising phase C1, CL, Tollhouse Mudstone Formation

Fig.5.13. Summary paragenesis for the Great Orme and the North Wales Platform (Burial curve modified from Al-Fadel 1983) (See also Appendix 6)
Fig. 5.14. Schematic summary of the cycles observed on the North Wales Platform that show overall upward shallowing, regressive trends observed within an overall Dinantian transgression. Llangollen = proximal- peritidal, Trefor Rocks; Great Orme = platform margin, Summit Limestone Formation.

Fig. 5.15. Summary of palaeoenvironments and environmental evolution
for the outcropping Asbian and Brigantian strata based on field and petrographical observation from the Great Orme, EISB = East Irish Sea Basin. The coloured boxes represent the positions of different key locations within the North Wales palaeogeography and relate to the corresponding idealised upward shallowing cycles at these locations.

**Tables**

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<th>Morphology</th>
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<td>Fe oxides</td>
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### Chapter 5. Sedimentation and diagenesis

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</thead>
<tbody>
<tr>
<td>C12</td>
<td>Blocky</td>
<td>Non luminescent – bright high frequency zonation</td>
<td>Sweeping</td>
<td>Limpid-turbid</td>
<td>Undifferentiated</td>
<td>Chalcopyrite</td>
<td>Extensional veins</td>
</tr>
<tr>
<td>C13</td>
<td>Bright orange-yellow</td>
<td>Unit</td>
<td>Turbid</td>
<td>Undifferentiated</td>
<td>Chalcopyrite?</td>
<td>Secondary vug and fracture</td>
<td></td>
</tr>
<tr>
<td>C14</td>
<td>Dull- orange yellow, etched</td>
<td>Unit</td>
<td>Limpid-turbid</td>
<td>Undifferentiated</td>
<td>Chalcopyrite?</td>
<td>Secondary vug and fracture</td>
<td></td>
</tr>
<tr>
<td>C15</td>
<td>bright orange yellow, etched</td>
<td>Unit</td>
<td>Limpid-turbid</td>
<td>Undifferentiated</td>
<td>Chalcopyrite?</td>
<td>Secondary vug and fracture</td>
<td></td>
</tr>
<tr>
<td>C16</td>
<td>Medium dull orange</td>
<td>Unit</td>
<td>Limpid-turbid</td>
<td>Undifferentiated</td>
<td>Chalcopyrite?</td>
<td>Secondary vug and fracture</td>
<td></td>
</tr>
<tr>
<td>C17</td>
<td>Xenotopic-planar-e</td>
<td>Very dull orange brown</td>
<td>Unit</td>
<td>Limpid-turbid</td>
<td>Undifferentiated</td>
<td>Secondary vug and fracture</td>
<td></td>
</tr>
<tr>
<td>C18</td>
<td>Bright orange high frequency zonation</td>
<td>Unit</td>
<td>Limpid-turbid</td>
<td>Undifferentiated</td>
<td>Chalcopyrite?</td>
<td>Secondary vug and fracture</td>
<td></td>
</tr>
<tr>
<td>C19</td>
<td>Non luminescent-bright high frequency zonation</td>
<td>Unit</td>
<td>Limpid-turbid</td>
<td>Undifferentiated</td>
<td>Secondary vug and fracture</td>
<td></td>
<td></td>
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**Table 5.1. Summary of the petrographic characteristics for the cements on the Great Orme, North Wales Platform**
**Chapter 5**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Formation</th>
<th>$\delta^{18}$O VPDB</th>
<th>$\delta^{13}$C VPDB</th>
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<tr>
<td>Calcite (Vein)</td>
<td>Great Orme Lmst</td>
<td>-6.65</td>
<td>1.81</td>
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<tr>
<td></td>
<td>Toll house Mudstone (G. Orme)</td>
<td>-8.31</td>
<td>2.17</td>
</tr>
<tr>
<td></td>
<td>Great Orme Lmst</td>
<td>-6.98</td>
<td>1.09</td>
</tr>
<tr>
<td>Whole rock (WR)</td>
<td>Summit Lmst (G. Orme)</td>
<td>-4.62</td>
<td>2.61</td>
</tr>
<tr>
<td></td>
<td>Bishops Quarry Lmst (G. Orme)</td>
<td>-5.00</td>
<td>2.21</td>
</tr>
<tr>
<td></td>
<td>Pier Dolomite (G. Orme)</td>
<td>-6.14</td>
<td>2.79</td>
</tr>
<tr>
<td>Dolomite whole rock (WR)</td>
<td>Pier Dolomite (G. Orme)</td>
<td>-7.28</td>
<td>3.21</td>
</tr>
<tr>
<td>Zebra dolomite</td>
<td>Pier Dolomite (G. Orme)</td>
<td>-6.76</td>
<td>2.56</td>
</tr>
<tr>
<td></td>
<td>Pier Dolomite (G. Orme)</td>
<td>-6.97</td>
<td>2.54</td>
</tr>
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</table>

*Table 5.2. Summary of stable isotopes, stable isotope values are reported to the VPDB standard*
### Table 5.3. Summary of trace element geochemistry

<table>
<thead>
<tr>
<th>Trace elements</th>
<th>Mg (ppm)</th>
<th>Fe (ppm)</th>
<th>Sr (ppm)</th>
<th>Mn (ppm)</th>
<th>Measuring device</th>
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</thead>
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<tr>
<td>D1</td>
<td>267.6</td>
<td>14.6</td>
<td>0.06</td>
<td>5519.1</td>
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<tr>
<td></td>
<td>268.3</td>
<td>11.3</td>
<td>63.6</td>
<td>5532.9</td>
<td>ICP-MS</td>
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<tr>
<td>Average</td>
<td>267.9</td>
<td>12.9</td>
<td>31.8</td>
<td>5526.0</td>
<td>Microprobe</td>
</tr>
<tr>
<td>D1-D2</td>
<td>247.9</td>
<td>12.5</td>
<td>0.06</td>
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<tr>
<td></td>
<td>344.0</td>
<td>21.5</td>
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<td>7601.9</td>
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<tr>
<td>Average</td>
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<td>32.9</td>
<td>5237.9</td>
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</tr>
<tr>
<td>D3</td>
<td>82.7</td>
<td>3.1</td>
<td>0.03</td>
<td>1.7</td>
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<td></td>
<td>180.7</td>
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<td>24.9</td>
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<td>12.4</td>
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<tr>
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<td>-</td>
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<td>-</td>
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</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Microprobe</td>
</tr>
<tr>
<td>D6-D7</td>
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<td>8.1</td>
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</tr>
<tr>
<td></td>
<td>56.2</td>
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<tr>
<td>Average</td>
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<td>13.0</td>
<td>18.4</td>
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<tr>
<td>WR D</td>
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<tr>
<td></td>
<td>157.2</td>
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<td>Microprobe</td>
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<tr>
<td>Ca</td>
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<td>0.09</td>
<td>0.5</td>
<td>0.03</td>
<td>ICP-AES</td>
</tr>
<tr>
<td>WR Lmst</td>
<td>65.6</td>
<td>9.5</td>
<td>0.6</td>
<td>1.4</td>
<td>ICP-AES</td>
</tr>
<tr>
<td>Basin</td>
<td>-</td>
<td>31.7</td>
<td>0.5</td>
<td>0.3</td>
<td>ICP-AES</td>
</tr>
</tbody>
</table>

Chapter 5. Sedimentation and diagenesis
Chapter 6: Multiscale Structural Evolution of the North Wales Platform Margin, Insights from the Great Ormes Head, UK
Chapter 6

6.0 Multiscale Structural Evolution of the North Wales Platform Margin, Insights from the Great Ormes Head, UK

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Keywords: Fracture; Diagenesis; Dinantian; North Wales Platform

Abstract:
The Lower Carboniferous North Wales Platform is located on the southern margin of the East Irish Sea Basin and formed during a period back-arc extension. Platform formation was followed by multiple subsidence and uplift events during which, fault/fracture movements were focused on deep seated Caledonian trends. These tectonic events and associated fluid expulsion gave rise to a complex structural paragenesis, which is outlined in this study. Early opening mode fractures (N-S) formed during structural diagenetic stage 1; these fractures are evident throughout the study area, are located proximal to bedding surfaces and host isopachous and syntaxial marine-meteoric calcite cements. This ongoing background fracturing occurred throughout the early diagenetic history of the North Wales Platform. Cementation during this early stage of burial occurred at depths of <300m and before chemical compaction. N-W and E-W fractures formed during the onset on NNW-SSE Variscan compression in structural diagenetic stage 2. Stage 2 fractures host shallow to moderate burial calcite and dolomite cements. Structural diagenetic stage 3
occurred with increasing compression that resulted in continued background fracturing and reactivation of Caledonian trend lineaments with a strike-slip component. At this time the Carboniferous (Namurian) sediment in the East Irish Sea basin was buried to depths of ~1-1.5km. Tectonism caused by the Variscan Orogeny and/or convection may have provided the mechanism for fluid movement during deep burial. Diagenetic stage 4 occurred during maximum compression creating folds displaying flexure slip and brittle deformation, continued fracturing, fault movement and emplacement of carbonate burial cements and MVT mineralisation (galena, sphalerite). The platform succession was subsequently re-buried during the end Permian until the Late Cretaceous-Early Tertiary after which it was exhumed in a second uplift event (Alpine Orogeny). This second event is associated with WNW-ESE and E-W compression and related fracturing, fluid flow and copper mineralisation, which characterises structural diagenetic stage 5. The final stage (6) is defined by relaxation and the production of barren, open mode fractures (E-W and NW-SE) that cross-cut all previous structural and diagenetic features.

6.1 Introduction
The North Wales Platform and adjacent East Irish Sea Basin were established during a period of back-arc extension in the Lower Carboniferous (Gawthorpe, 1989). The North Wales Platform succession comprises Asbian and Brigantian fractured carbonates and is one of several Lower Carboniferous platforms within the UK. The contemporaneous Derbyshire and Askrigg Platforms have been fully characterised and have well constrained structural and fluid flow histories by comparison (e.g. Coleman et al., 1989; Ixer & Vaughan, 1993; Hollis, 1996). The well exposed Asbian-Brigantian succession on the North Wales Platform provides an excellent opportunity to study the relationship between structure and diagenesis. The conventional approach for describing the structural evolution has so far included field mapping and extrapolation from offshore seismic scale studies (Nichols, 1968; Williams & Eaton, 1993).
It is recognised that fluid flow is an important process related to structural deformation and can result in the mineralisation and cementation (Laubach et al., 2010). Therefore, holistic basin analysis approaches can be adopted to understand fluid flow and its relation to structural reactivation through time. In particular, faults and fractures can act as important flow conduits for diagenetic fluids, which can result in precipitation of cements or dissolution of the surrounding host rock. This cross-disciplinary approach termed structural diagenesis provides the opportunity to date fault and fracture movement, rates of fracture growth and locate potential open fracture systems (op. Cit.). This approach is being increasingly used to improve the predictability of reservoir quality distribution in producing hydrocarbon reservoirs, and can also be applied to water management and mineral exploration.

Previous studies of the North Wales Platform and East Irish Sea Basin have focused upon stratigraphic, sedimentological and paleontological description (e.g. Hind & Stobbs, 1906; Warren et al., 1984, chapter 5, pp 107-127; Davies et al., 2004 and references therein). The structural history has not been so thoroughly addressed and many questions remain. In particular, (a) What was the kinematic evolution of the platform? (b) What events controlled fluid flux? (c) What is the relationship between diagenesis, structure and the wider basin evolution?

This study focuses upon the Great Orme, a small peninsula on the North Wales coast, UK. The Great Orme provides excellent exposure of Lower Carboniferous limestone and dolomitised limestone, in which the relationship between structure, sedimentation and diagenesis has been investigated. The structural history of the Great Orme has previously been described by Morton (1898); Nichols (1968) Oldham (1987) and Williams & Eaton (1993). However, the precise timing and mode of movement are difficult to establish from the limited field observation and 2D seismic alone. Furthermore, no genetic relationship between faulting, fracturing cementation and/or mineralisation has been described.

In this paper we integrate multiscale field, petrographic, stable isotope and trace element geochemical analyses to delineate the structural evolution of the Great Orme. The study aims to 1) Describe the structural features
Chapter 6. Structural evolution

encountered on the Great Orme at a variety of scales (i.e. kilometre to millimetre scale); and group them based on style, cross-cutting relationship and domain 2) Determine the relationship between the structure and diagenesis 3) Establish the relative timing of the main phases of deformation and summarise within a schematic kinematic model for the evolution of the Great Orme.

6.2 Geological and Structural Setting
The North Wales Platform was one of a number of Lower Carboniferous carbonate platforms that formed within a back-arc extensional setting during the Lower Carboniferous (Fraser & Gawthorpe, 1990). At this time, the equatorial position of the UK in combination with structurally controlled, palaeo-geographic highs produced optimum conditions for carbonate sedimentation and led to the development of carbonate build-ups (Waters & Davies, 2006). The North Wales Platform developed as a carbonate ramp in the Lower Dinantian and evolved into a rimmed-platform during the Late Dinantian (Somerville et al., 1989). During the mid-Carboniferous (Namurian) carbonate production ceased due to the cessation of rifting, leading to the onset of thermal sag subsidence (Leeder, 1982; Walkden, 1987; Walkden & Walkden, 1990). This, and an associated increased flux of siliciclastic sediments within fluvio-deltaic systems sourced from the southerly Wales-Brabant Massif, led to termination of carbonate platform growth. The same switch in sedimentation style occurred across the north of England (Aitkinhead et al., 1985).

The North Wales Platform was subjected to multiple phases of faulting and folding from the Carboniferous through to the Tertiary which was controlled by deep seated, pre-Carboniferous lineaments (Fraser & Gawthorpe, 1990; Turner 1997). Structures dissecting the North Wales Platform follow predominantly Caledonian trends (N-S, NE-SW and an E-W structural grain) and are observed at a regional and local scale (e.g. Great Orme - Nichols, 1968; Wilson, 1968; Tremlett, 1970; Bassett, 1984; Lee et al., 1990; Williams & Eaton, 1993) (Figure 6.1). The Great Orme headland is situated at the northern end of the Menai Straits Fault System, a Caledonian shear zone, and
is bounded by the Aber-Dinlle Fault to the south and the Dinorwic Fault to the north (Figure 6.1); both these major faults had been active since the Cambrian (Needham & Morgan, 1997).

The Menai Straits or Conwy Valley Fault System is a network of NE-SW trending faults (Figure 6.1), which were mainly active from the onset of the Caledonian Orogeny (Tremlett, 1970; Campbell et al., 1985). It originated as a strike-slip system, which was later reactivated with normal movement (Reedman et al., 1984; Woodcock, 1988; Gibbons, 1990). Adjacent fault systems in North Wales such as the Clwyd Valley and Prestatyn Fault Systems display similar trends and evidence for activation and movement contemporaneous with the Conwy Valley faults (Davies et al., 2004). Between the major faults (Aberdinlle, Dinorwic and Berw Faults) within the Conwy Valley system, subsidiary faults have developed. The faults are up to 5km in length and are orientated perpendicular and conjugate to these major faults. One of these smaller fault systems can be observed on the Great Orme (Nichols, 1968).

Subsequent fault reactivation took place during the Variscan Orogeny, which occurred across the south of England through to mainland Europe throughout the Carboniferous, with basin inversion initiated in the Late Carboniferous (Westphalian to Stephanian; Corfield et al., 1996). In North Wales Variscan deformation resulted in folding, NE-SW and N-S faulting, and sinistral transpressive regimes (op. Cit.). In northwest Wales the folding resulted in depositional thickness variations of the Carboniferous carbonate succession. Thus, across the Aber-Dinlle Fault, a thicker succession is measured from the Great Orme to the adjacent Gloddaeth Syncline (Williams & Eaton, 1993). This became more pronounced as further inversion during the Variscan Orogeny culminated in erosion of the Gloddaeth Syncline (Williams & Eaton, 1993; Needham & Morgan, 1997).

Post-Carboniferous tectonic activity included extension during the Permian to the Jurassic and the Alpine Orogeny during the Tertiary, which also reactivated faults within North Wales but this time with a more east-westerly trend (Wilson, 1968; Reedman, 1984).
6.3 Great Orme: sedimentation and stratigraphy

The Great Orme is a headland, 4km long, 0.8km wide and 200m in height, which consists of exposed Asbian and Brigantian sediments. The outcrop comprises five stratigraphic units as defined by Warren et al. (1984) and references therein (Figure 6.2, 6.3). The stratigraphic units are characterised by upward-fining deposits capped by exposure surfaces and the development of proto-soil. The depositional pattern has been attributed to cyclicity that is potentially equivalent to that described further east on the North Wales Platform (Somerville et al., 1989), on Anglesey to the west (Davies, 1984) and across age-equivalent platforms in northern England (e.g. Walkden & Berry, 1984; Horbury, 1987, Vanstone, 1996). On the Great Orme the Asbian to Brigantian succession is dominated by well-bedded wackestones to packstones although interbedded mudstone, grainstones and rare siliciclastic units also occur (Figure 6.3). Overall, sedimentation is interpreted to represent stacked, metre-scale cycles of platform margin and open marine platform top and platform interior intertidal facies (Juerges et al., in prep, chapter 5).

6.4 Paragenesis

A chronological sequence of diagenetic products on the Great Orme has been established through the superposition and cross-cutting relationships determined by field and petrographic observation. These phases are summarised briefly here and in Table 1, and have been described in detail by Juerges et al., (in prep and Chapter 5) (See also Appendix 3, 4, 5 and 7).

The first cement phases observed on the Great Orme are isopachous, fibrous calcite M1, syntaxial cements SC1-SC3 and pore-occluding C4. These cements have been observed within all formations except for the Pier Dolomite Formation. They occur primarily within interparticle porosity of grainstone facies and are nucleated on crinoid and echinoid fragments. They are volumetrically the most abundant matrix pore-filling cements observed across the North Wales Platform and occlude the majority of primary porosity. It is suggested that they formed in the marine-meteoric environment (Juerges et al., in prep, chapter 5).
Within the Pier Dolomite Formation the first cement and matrix replacive phases include dolomite D0-D2. They are present as fabric destructive, xenotopic to euhedral (rhombic) interlocking mosaics. There is no obvious relationship with the faults and fractures.

**Calcite C5-C9**
Calcite cement is the most frequently observed fracture fill observed on the Great Orme. Calcites cements occlude all fracture orientations, but occur in the greatest abundance within fractures striking N-S. From petrographic analysis C5-C9 calcite cements display columnar and blocky crystals forming a variety of drusy, massive and equigranular textures. They are differentiated on the basis of their luminescence characteristics (Table 1) and sequentially overgrow one another within single fractures.

**D3-D5**
D3-D5 dolomite cements have been identified within fractures with a dominant N-S orientation and infilling zebra textures. The phases are observed within the Pier Dolomite Formation and to a lesser degree within stratigraphically higher intervals within faults and large joints. D3-D5 form coarsely crystalline, rhombic saddle dolomite crystals that display crack-seal and bridging textures. These phases are mainly restricted to the fractures, are in optical continuity with the host-rock dolomite within the Pier Dolomite Formation but also display overprinting. This suggests that D3-D5 precipitated from the same or compositionally similar fluids during progressive fracture related fluid flow. Moreover, clasts of host-rock dolomite float within multiple phases of dolomite vein cement with crack-seal textures close to faults within the Pier Dolomite Formation, suggesting multiple fracture reactivations.

**D6-D7**
D6-D7 dolomite cements are found within N-S and NE-SW oriented fractures. They are also found in minor volumes within structures striking NW-SE, especially where they cross-cut earlier dolomite filled fractures and occasionally exploiting calcite filled fractures (C5-C9) within the Great Orme.
Limestone Formation. In this case, rhombic crystals of D6-D7 dolomite replace C5-C9 calcite cements and adjacent host rock limestone with rhombic crystals. This alteration persists for up to 1cm away from the fractures. Phases D6 to D7 have not been observed within faults during the course of this study.

*Calcite C10-C13*

*C10 to C13* calcite cements occlude fractures that strike NE-SW. They comprise blocky crystals forming a variety of drusy and massive textures. Staining indicates the calcite is predominantly ferroan. CL reveals bright orange to yellow luminescence with weak to no zonation. C13 cements are intergrown with chalcopyrite. In addition, secondary copper minerals and bitumen has been observed within these later diagenetic phases.

*Calcite C14-C19*

*C14 to C19* calcite cements are located within fractures and secondary porosity. They display a variety of luminescent characteristics and textures that may indicate precipitation during burial and subsequent uplift (chapter 5). Further indication of surface related diagenesis and the potential involvement of meteoric fluids include etching and dissolution and de-dolomitisation. The absence of reactivation textures such as cement bridges and crack-seal suggest that the cements were passively precipitated into open voids.

*Quartz*

Quartz is the final cement phases encountered within fractures on the Great Orme. It is found primarily within low angle fractures that are orientated E-W. The volume of quartz is very low in comparison to earlier carbonate cements. It forms blocky to columnar crystals of up to 2mm in length.

**6.5 Techniques**

Initial analysis consisted of aerial image interpretation in which structural lineaments (down to a metre scale resolution), were identified and mapped, and areas of interest for detailed field study were defined (Appendix 2).
Five key, accessible, locations were described using sedimentary logs and scan-lines, perpendicular to faults and large fracture systems recording the orientation, geometry, fill and cross-cutting relationships of structures of differing scales. The sections were systematically sampled across fault and fracture zones (Figure 6.3).

From the samples, 45 25µm thick polished thin sections were prepared and half stained with alizarin red S and potassium ferrocyanide following Dickson (1965). The staining allowed magnesium and calcium carbonate cements to be differentiated and also phases of non-ferroan and ferroan cement. The polished sections represent facies, micro-structure and diagenetic products at incremental distances from faults and through-going fractures. These were then analysed petrographically using plane light techniques and cathodoluminescence. Cathodoluminescence (CL) was achieved using a Cambridge CCL Cold Luminoscope 8200 mk3, operated at an accelerating voltage of 10Kv, a vacuum of 2 torr and gun current of 300Kv. Photographs were taken using a Progres C10 Laser Optik System.

6.6 Results

From field and petrographic analysis, several structural features have been identified, including fractures, faults, folds and stylolites. For the purpose of this study veins refer to cemented fractures, whilst fractures are open (i.e. uncemented), unless otherwise stated. A chronological sequence of events has been constructed by using the cross-cutting relationships of these different structural features and incorporating diagenetic observation. These are described below in approximate paragenetic sequence:

*Planar fractures*

Infrequent planar fractures hosting a partial fill of fibrous M1 (see chapter 5, Juerges et al., in prep, and Table 1) calcite cement have been recorded below erosion surfaces and palaeosols within the Great Orme Limestone Formation. The fractures are bedding confined, orientated perpendicular to bedding, up to 5cm long and 0.5cm wide. These fractures have variable strike directions and terminate within the beds. The relationship with stylolites is unclear. However,
the position close to erosion surfaces and the fibrous morphology of the cements are suggestive of formation during early diagenesis. The lack of luminescence may indicate a marine origin as opposed to a meteoric origin, which are usually characterised by concentric cement zones indicative of fluctuating water chemistries, variation in Eh and redox boundaries, and/or thermochemical controlling on precipitation (Walkden & Berry, 1984; Emery & Dickson, 1989).

**Bed parallel stylolites**

Bed parallel stylolites and compaction-enhanced bedding planes have been observed across the Great Orme (Figure 6.4). The stylolites have concentrated insoluble residue along their length and, within the Pier Dolomite Formation, saddle dolomite crystals. These compactional features display low amplitude (<1cm high) undulose seams that are laterally extensive and extend the length of the outcrops. The bed parallel character of the stylolites is interpreted to indicate formation as a result of burial compaction.

**Background fracturing**

Extensional fractures throughout the Great Orme have been observed with a variety of strike orientations (Figure 6.4). They occur as vertical bedding and non-bedding confined fractures and close to normal faults have also been observed at angles as low as 20°. The fractures contain partial and complete fill of calcite cement zones C5-C9 (Juerges et al., in prep, chapter 5). The calcite cements are present in all fracture orientations, but occur in particularly high abundance within fractures striking N-S. From petrographic analysis, calcite cements display columnar and blocky crystals forming a variety of drusy, massive and equigranular textures. Stable isotope values were not obtained due to the very small volume of material available.

Due to their ubiquitous nature, lack of evidence for a direct relationship with large scale structures, and cement phases and characteristics the fractures are interpreted to have formed as background fracturing during burial. More specifically, the host-rock limestone was brittle due to precursor cementation.
and fracturing resulted from overburden pressure and potentially the onset of early but minor folding (e.g. Saller, 1996; Bazalgette et al., 2010).

**Bed confined fractures and veins with host-rock breccia ($F_a$ and $F_b$)**

Two sets of bed normal planar fractures have been identified. The first comprises barren, regularly spaced, high density vertical fractures hosted by interbedded mudstone within the Bishops Quarry and Great Orme Limestone Formations (Figure 6.4). These fractures occur within beds that are up to 20cm thick, <0.5cm wide, 20cm long and strike N-S and NE-SW. The second set includes planar veins hosting dolomite (D3-D5) and calcite cement within the Pier Dolomite Formation. These fractures have been observed within mudstone and wackestone facies on the limbs of folds in close proximity to bed parallel veins (see below). The fractures are orientated E-W, dip between 45 and 90° from bed parallel, extend to the height of the bed (30cm) and are between 0.5cm and 20cm wide. The vein fill contains angular clasts of host-rock limestone, up to 5cm in diameter, and has multiple cement fills. In addition, the fractures cross-cut and are cross-cut by bed parallel stylolites. Fracture set (a) is consistent with purely extensional or tensile fractures within consolidated sediment (e.g. Schöpfer et al., 2011 and references therein). Set (b) also indicates tensile fracturing although the larger apertures, cementation and floating host-rock breccia also suggests high pressure hydrofracturing (e.g. Sibson, 1985). The cross-cutting relationship with the stylolites places a pre to maximum compactional timing of the fracturing, with stylolitisation interpreted to take place at depths of approximately 300m (Sibley & Gregg, 1982).

**Bed parallel veins**

Two sets of bed parallel veins have been observed: (1) laterally extensive veins at dolomite-mudstone bed boundaries in the Pier Dolomite Formation and (2) veins extending from mixed mode faults at limestone-mudstone bed boundaries within all the formations (Figure 6.4). Bed parallel veins are <3cm thick, host dolomite (D3) and calcite cement and display evidence for multiple opening and sealing events in the form of wall rock inclusions. The veins
extend for several meters, cross and are cross-cut by bed parallel and bed normal *en echelon* veins. Kinematic indicators include deformation and stretching of vein cements and pinch-outs resulting in discontinuous vein fill. Moreover, they cut and are cross-cut by bed parallel and bed normal stylolites. This places a relative timing of between pre to maximum burial compaction and pre-maximum compression. The veins formed as opening mode fractures that filled with carbonate cement and are consistent with the maximum stress orientated bed parallel or oblique to bedding. The veins are not common and primarily located within the Pier Dolomite Formation and situated at mudstone- dolomite/tight limestone bed boundaries which are interpreted to be the weakest planes within the lithified and/or crystalline host succession (e.g. Brown & Moore, 1993; Gammon et al., 2012).

*Bed parallel en echelon vein arrays*

Bed parallel and sub-parallel vein arrays are observed within the Pier Dolomite Formation. The arrays host dolomite (D3-D5), are not bedding confined and range in width from <0.5cm to 1cm thick. The arrays display an apparent dip of 35° N or are bed parallel and linked tension gashes step upwards to the right (north) indicating maximum stress parallel and sub-parallel to bedding (N-S) (6.4 and 6.5). The pattern of stepping and vein opening indicate sinistral movement, which is consistent with reverse slip of overlying beds.

*Zebra textures*

Two sets of zebra dolomite textures have been identified from field observations. The first set Zₐ are observed mainly in the Pier Dolomite Formation, although they are also visible within the stratigraphically higher Great Orme Limestone Formation (Figure 6.5 and 6.6). Within the Pier Dolomite Formation the Zₐ have no clear relationship to bed normal faults. The second set, Zₐ, are observed in the Pier Dolomite Formation and within the overlying Great Orme Limestone Formation these occurrences are only situated directly adjacent to faults and large through-going fractures (see below). The zebra textures, Zₐ and Zₐ, comprise alternating bands (up to 2mm
thick) of opaque white crystalline and buff coloured matrix replacive and pore-filling dolomite (D3). The veins extend for up to 1m from faults, fractures and/or bed planes, are between bed-parallel and 20° from bed parallel and are arranged in a planar, stacked pattern or en echelon arrays. The zebra textures extend laterally for up to 1m and 30cm in height with rock bridges visible between discontinuous zones of zebra textures. From the top of bedding surfaces the zebra textures appear chaotic with rounded and etched dolomite host-rock clasts floating in dolomite cement, suggesting hydrobrecciation. The dolomite cements hosted within the zebra textures display coarse saddle crystals, which are also evident in N-S, NE-SW and bed parallel fracture systems across the Great Orme (Figure 6.7).

Folds
Folds on the Great Orme range in scale from 200m (SW Great Orme) to up to kilometre scale (syncline affecting the whole succession) are asymmetric and are orientated NE-SW to WSW-ENE. The plunge of the folds was not determined in the course of this study.

Fold limb fractures and Brittle deformation
Fold limb fractures have been observed to extend upwards from bedding planes and are hosted by fine grained facies (mudstone-packstone) (Figure 6.6). The fractures are barren, open and arcuate, orientated sub-parallel to bedding and situated on fold limbs. These fractures are observed within the Tollhouse Mudstone Formation and at the base of the Great Orme Limestone Formation on the limb of an antiform, on the NE side of the Great Orme, where the whole Great Orme, Asbian-Brigantian Succession has been folded. They extend upwards from bedding planes in an arcuate manner and dip up to 20° from bed parallel. The fractures range in length from 10cm to 30cm and in width from 0.2cm to 0.7cm, tipping out within the host bed. The fractures are interpreted as brittle deformation during folding.

NE-SW, NW-SE and N-S Faulting and associated fracturing
Faults striking NE-SW are evident from aerial image analysis and field observation (Figure 6.6 and 6.7). For the most part they are located to the north and south-west of the Great Orme, are up to 3m wide and traverse the width of the Great Orme (2km). These structures dissect all visible outcropping strata. Cements associated with the faults include calcite (C5-C16) and quartz but primarily dolomite (D3-D7). The internal architecture of the faults displays mosaic breccia (Figure 6.7). NE-SW fractures are visible within all lithologies at all stratigraphic horizons. Fractures fills include dolomite and calcite. The fractures display passive and drusy textures. They are up to 1m+ in length and 3cm in width. They often display evidence of offset. 

NE-SW and N-S orientated faults and fractures are the most prominent observed around the Great Orme. N-S structural orientations are apparent within all lithologies, stratigraphic units and ranges from micro to kilometre scale. N-S structures host dolomite and calcite cements, which display drusy, passive or bridging textures. Within the Pier Dolomite Formation there are also large, rounded and etched dolomite host-rock clasts that float within massive dolomite and later calcite cemented veins extending away from N-S faults (Figure 6.7). The multiple cement fill and nature of the clasts suggests hydro-brecciation with multiple reactivations of the veins. The dolomite phases within N-S fractures overprint the calcite and adjacent host rock limestone with rhombic crystals. This alteration persists for up to 1cm away from the fractures. Kinematic indicators for faults, such as slickenside striations, indicate predominantly mixed mode or normal movement, whereas fractures don’t tend to display evidence of offset. In addition, zebra textures are associated with NE-SW and N-S oriented fractures throughout the Great Orme. The zebra textures extend away from these structures for up to 2m and are evident within all formations (Figure 6, 7).

The orientation and style of deformation and the formation of the faults (mixed mode faults and strike-slip reactivation) and associated open mode fractures are consistent with N-S compression. In addition, the similarity in cement paragenesis suggests that the fault and fracture networks were active at the same time and may have been connected.
**Vertical stylolites**

Low amplitude, non bedding confined stylolites, orientated perpendicular to bedding occur on fold limbs and in close proximity to normal and mixed mode faults (Figure 6.6). They strike roughly E-W and extend for up to 2m. The stylolites are interpreted as structural stylolites, orientated perpendicular to the direction maximum stress.

**Minor calcite filled fractures**

Calcite filled fractures that cross-cut bed normal stylolites occur within the Tollhouse Mudstone and Great Orme Limestone Formations (Figure 6.6 and 6.7). They exhibit variable orientations, lengths of up to 20cm and are <0.5cm wide. The fractures are situated in close proximity to normal and mixed mode faults and decrease away from the fault zone. The fractures are interpreted as parallel and oblique structures along faults (e.g. Petit et al., 1999).

**E-W faults and fractures**

E-W faults have primarily been identified from aerial image analysis (Figure 6.8). At outcrop, E-W structures can be seen behind the south-west Toll House (SH 7680 8245). The fault and surrounding damage zone is located within the Pier Dolomite Formation and extends to the height of the outcrop (10m). The fault dips at 45° and displays slickenside striations within calcite cements on the footwall surface. This kinematic indicator shows reverse movement. Other cements associated with the fault include quartz cementation. Quartz is hosted by small fractures and vugs connected and directly adjacent to the fault. Further, the deformation surrounding the fault shows a mesh-work of cemented fractures resulting in ‘fish’ or isolated pods of rock with the long axes orientated in the dip-direction of the fault (Figure 6.8). E-W orientated fractures occur across the Great Orme but in much lower abundance than earlier fracture sets. The fractures primarily contain calcite cement (C10 to C13), small chalcopyrite crystals 200µm to 1000µm in size with secondary copper mineralisation and bitumen. Where the fractures cross-cut earlier dolomite-filled fractures phases D6-D7 occur. The final phase in the paragenesis includes minor volumes of quartz. The change in dominant
fault and fracture orientation suggests a change in major stress direction, whilst change in cement and mineral assemblage indicates a change in fluid source and/or flow pathways. The E-W structures are observed along with reactivation of N-S trends, which is consistent with N-S extension or E-W compression.

**Barren fractures**

The last structural features identified by the cross-cutting relationships are barren, open fractures. They are predominantly observed in the Pier Dolomite Formation. The fractures are vertical, non bedding confined, cross-cut all previous features, are oriented E-W and NW-SE. The fractures extend for several meters and are between 0.5cm and 1cm wide. The lack of cement and opening mode nature of the fractures that cross-cut all previous fractures sets and structures indicates extension with no associated fluid flow.

**6.7 Discussion**

A complex structural history has been identified from the cross-cutting relationships between structural features and superimposition of cements (figure 6.9, Table 2). The structural and diagenetic elements have been grouped into structural diagenetic stages based on their relationships to each other and their relative timing. These include 1) background deformation during early burial, 2) deep burial, 3) onset of Variscan compression, 4) main stage Variscan compression, 5) re-burial and Tertiary uplift and 6) relaxation.

**Structural diagenetic stage 1**

The first stage of structural deformation spans the earliest phases of syn-depositional fracturing to the onset of chemical compaction (Figure 6.10). Based upon Sibley & Gregg (1987), this is interpreted to occur at burial depths of <300m. The earliest fractures are sub-vertical to vertical open mode fractures, orientated normal to bedding and occluded by non-luminescent, fibrous and bladed calcite cement indicative of precipitation within a marine and/or meteoric environment (Juerges *et al.*, in prep, chapter 5). These fractures occur within undolomitised Asbian limestone beneath exposure
surfaces and palaeosols (e.g. Great Orme Limestone Formation). Dinantian, sedimentation took place in a back-arc extensional regime and deposition was partially controlled by active, syn-depositional tectonism (Leeder, 1988, Frazer & Gawthorpe, 1990). However, observations of syn-sedimentary deformation have been limited most likely due to the early cementation creating a rigid framework. Sediment was periodically subjected to exposure as a result of tectonically and eustatically controlled fluctuations in relative sea level. This is evidenced by several red palaeosol horizons and led to the ingress of meteoric fluids and extensive syntaxial pore-occluding cements (Juerges et al., in prep, chapter 5, Al-Fadel, 1983). The structural regime and diagenetic environment would have provided ample opportunity for the fractures and early cements to form.

During this early phase of diagenesis, there is good paragenetic evidence from field and petrographical data that dolomitising fluids were circulating within shoaling facies at the platform margin (e.g. Pier Dolomite Formation) (Juerges et al., in prep, chapter 5). This earliest phase of dolomitisation is recorded by matrix replacive and pore-occluding cements (D0 to D2) which reduced porosity and consolidated sediment within the Pier Dolomite Formation. This matrix-replacive dolomite is cross-cut by stylolites that host coarsely crystalline saddle dolomite crystals. Bed parallel stylolites and solution seams also occur within the younger formations that overly the Pier Dolomite Formation, principally within the mudstone and wackestone facies and along bedding planes indicating the onset of chemical compaction. The early cementation within the coarse grained facies provided a rigid framework but also increased the brittle nature of the rock favouring fracturing. This is evident where the fractures control the distribution of D2.

**Structural diagenetic stage 2**

Stage 2 is a continuation of stage 1 and records ongoing burial and subsidence (Figure 6.10). Prior to the onset of Stage 2, occlusion of porosity by marine, meteoric and early burial calcite and dolomite cements had reduced the number of potential fluid flow pathways and modified the mechanical properties of coarse packstone and grainstone beds, essentially
creating low porosity/low permeability brittle beds. The resulting contrast in competency between well cemented and fine grained (mudstone/wackestone) beds resulted in a heterogeneity of deformation styles. Planar and *en echelon* extensional veins, restricted to fine grained wackestone facies and partially dolomitised limestone occur normal to bedding. The first set of fractures \( (F_a) \) comprises a high density of barren, open mode (mode 1) fractures orientated normal to bedding. The mode and lack of fracture fill suggests sediment was consolidated during formation. Further, the direction of opening implies the maximum stress direction \( (\sigma_1) \) was orientated normal to bedding. Therefore, it is most likely that the fractures formed during burial when the overburden stress was able to exceed the tensile rock strength resulting in brittle deformation (Reches, 1998). These fractures are cross-cut, and are cross-cut by, bed parallel stylolites, suggesting that they formed during ongoing subsidence and burial. The second fracture set \( (F_b) \) is confined to wackestone and partially dolomitised limestone beds within the Pier Dolomite Formation. The fractures contain angular host-rock breccias floating in dolomite and calcite cement. For these well cemented fractures to form, the host rock would have to have been consolidated at the time of fracturing. Moreover, the host-rock breccia that is supported by a massive cement fill \( (D_3 \text{ and later calcite}) \) indicates high pressures (potentially overpressured) during fracturing and is consistent with a dilation breccia as defined by Sibson (1985). Similar observations have been recorded for tensile fractures within well-bedded and fine grained facies in the Jabal Akhdar Mountains, Oman where localised overpressuring has been well illustrated (Hilgers *et al.*, 2006). The high pressures can be created by differential compaction, tectonic stresses, thermal expansion and diagenetic processes or a combination of these controls (Marquez & Mountjoy, 1996; Sibson, 2000). The evidence for a combination of compaction, diagenesis and possible tectonic stress is compelling. The initial dolomitisation would have driven dewatering through an increase in grain/crystal size, reduced porosity by replacing grainstone facies with interlocking mosaics and cementing pore spaces within all facies. Eventually the process of porosity reduction would exceed dewatering, thus increasing the internal fluid pressures at the pore
scale (e.g. Gammon et al., 2012). During burial, continued dolomite replacement in surrounding beds and lithification of the fine grained sediment would have reduced the ability for the sediment to expand and accommodate the increasing fluid pressure, providing further potential for overpressures to occur. As for the previous fracture set (F_a), the maximum stress would have been orientated normal to bedding and failure taking place when the tensile stress exceeded the strength of the rock. However, the cement-filled fractures do exhibit evidence for limited localised shear and slight rotation producing ‘S’ shaped veins (Figure 6.5).

The tensile fractures (F_b) are cross-cut by bed parallel veins that occur between mudstone-dolomite/dolomitised limestone bedding planes. Four models have been proposed by Hilgers et al. (2006) in order to explain bed parallel veins; (1) super hydrostatic pressures with σ_1 orientated parallel to bedding (2) the formation of dilational jogs related to shear (3) compression with effective confining pressure and resulting in the linking of en echelon fractures and (4) high pressures created when the tensile strength of a rock is larger than the differential stress such that the bed parallel veins and also F_b tensile fractures are controlled by high internal pressures. F_b fractures are only seen where there is a mechanical contrast between beds and there are no kinematic indicators, nor evidence based on the regional tectonic evolution, for a rotation in maximum stress from bed normal to bed parallel at this time.

Throughout the Lower Carboniferous, normal faulting led extensional reactivation of faults across North Wales, although a shear component has also been recognised (Coward et al., 2003). This is seen within the mixed mode faults on the Great Orme. Evidence from this study of reactivation after lithification, includes vertical and horizontal fault striations and a lack of variation in sediment thickness that would be expected across normal faults active during sedimentation (e.g. Fitches & Campbell, 1987; across the Bala Lineament: Gawthorpe et al., 1989). Furthermore, high-angle conjugate fault and fracture systems with brecciation confined to the fault zones have been witnessed on multiple scales from aerial image (km-scale) to petrographical (mm-scale). The location and geometry of subsidiary structures adjacent and
normal to the main NE-SW faults can be explained by local strike-slip fault movement on the Great Orme (Figure 6.9). To the east of the Great Orme, the Gloddaeth Syncline and the Clwyd Fault System (Waters & Davies, 2004) both display extensional – transtensional components with associated strike-slip subsidiary faults (Tremlett, 1970; Reedman et al., 1984; Williams & Eaton, 1993; Figure 5). On the Great Orme this Early Carboniferous extensional phase is represented by reactivation of deep seated faults (normal and strike-slip), subsidence and background fracturing, and characterises structural diagenetic stages 1 to 2. This is supported by cross-cutting relationship of the structures and the fracture hosted cements, which display more burial characteristics with each phase.

**Structural diagenetic stage 3**

Stage 3 is characterised by *en echelon* fractures parallel and sub-parallel to bedding, zebra fabrics \( (Z_a) \) and reactivated bed parallel fractures (mode II), with kinematic indicators suggestive of sinistral bed parallel shear. Therefore, there is a marked change during this stage from basin subsidence and deformation as a result of failure under maximum stress perpendicular to bedding, to a compressional regime (e.g. Jaeger, 1963; Petit et al., 1999) (Figure 6.10). Furthermore, the fractures that characterise Stage 3 are occluded by multiple phases of dolomite and calcite cements, indicating that there was active circulation of a large volume of diagenetic fluids during this time. In particular, where multiple *en echelon* veins have aligned at dolomite-dolomite bed boundaries large scale cement emplacement has occurred. These veins display evidence of shear in their arrangement and within their deformed dolomite cement fills. The zebra textures are interpreted as *en echelon* tensile fractures created during compression that resulted in slip along the bed planes. It is suggested that the fluids responsible for the cementation migrated along the bed planes and vertically via fractures. The textures also provide evidence of overpressuring with brecciation visible on the tops of dolomitised limestone beds. This is also consistent with the hydrobrecciation visible on the bedding surfaces and limited number of fracture-occluding cements. The direction of fracture opening suggests the maximum
stress was orientated parallel or oblique to bedding. These veins are interpreted as forming from flexural-slip along bedding planes during compression and elevated effective confining pressures (e.g. Teixell et al., 2000). Slip between beds could have been aided by thin interbedded mudstone and contrast in strength resulting in planar veins. However, where these interbedded mudstones are absent the beds would have been more consolidated and tensile stresses higher thus more likely to result in high pressure tensile fractures such as *en echelon* arrays and zebra textures. Moreover, the bed parallel planar, *en echelon* and zebra textures are observed on the fold limbs on both sides of the Great Orme and diminish away from or towards the core of the fold, a relationship with compression and folding. Zebra textures display self organisation with alternating inclusion bands of host-rock suggesting cementation during fracture opening and potential overpressuring (e.g. sheet cracks of Gammon et al., 2012). Alternative hypotheses have been considered for the formation of zebra textures such as the presence of a precursor algal lamina and displacement veins whereby the precipitating crystals do not need a void to precipitate into (Merino et al., 2006). Although it is difficult to reconcile the production of regular voids during burial, the repeated release of overpressured fluids could account for the temporary presence of voids, the close spatial relationship to faults and fractures, and the cross-cutting of beds. It is more difficult still to invoke a process of dissolution-precipitation with self displacement during burial and in light of the observed relationship to structure. Formation by crack-seal during overpressure has been suggested for a number of analogous occurrences (e.g. Boni et al., 2000; Gasparrini, 2003; Swennen et al., 2003).

The dolomite cements (D3) hosted by the *en echelon* fractures display interlocking mosaics and saddle dolomite, which is consistent with elevated temperatures during precipitation (Sibley & Gregg, 1987). N-S trending *en echelon* veins formed with multiple cement fills, crack-seal textures and dolomite bridging cements. The textures indicate multiple reactivations, and cement precipitation on fracture opening. The direction of maximum stress is consistent with N-S orientated compression, which is consistent with the
maximum stress orientation that would have developed during the onset of the Variscan Orogeny (Frazer & Gawthorpe, 1990).

**Structural diagenetic stage 4**

Stage 4 is characterised by brittle and dynamic fracturing and high angle faulting with associated zebra (Z_+) texture development, and characterises the ongoing structural deformation associated with Variscan Compression. It is differentiated from Stage 3 by the onset of N-S and NE-SW faulting (Figure 6.10).

Structural diagenetic stage 3 was characterised by pervasive fracturing, fluid mobilisation from Dinantian sediment in the East Irish Sea Basin and cementation associated with the onset of Variscan compression. By the onset of Stage 4, sediments had dewatered and both matrix and fracture porosity had been pervasively cemented by calcite and dolomite. With ongoing compression, deformation became focused along N-S and NE-SW trending faults and fractures. This trend was inherited from precursor Caledonian features (Nichols, 1968, Davies *et al.*, 2004). The faults are vertical or high angle, and display normal offset and horizontal striations suggesting normal faulting followed by reactivation with a strike-slip component.

Brecciation and multiple fault and fracture fills indicates several episodes of reactivation. The fact that both fault orientations have the same cement paragenesis indicates the N-S and NE-SW trending structures were active at the same time and were most likely connected. The internal architecture of the faults comprises slightly rotated mosaics of angular host-rock clasts within dolomite and calcite cement, consistent with dilation brecciation (e.g. Sibson, 1985; Tarasewicz *et al.*, 2005) and strike-slip faulting (Christie-Blick & Biddle, 1985; Sylvester, 1988). The breccia damage zone is of limited lateral extent indicating only periodic reactivation (a larger breccia zone would be expected if the faults were continuously active). Fault fish have been observed between the large scale strike-slip faults. The pattern arises where joints formed parallel and at low angle to the strike-slip faults and are cross-cut by joints at high angle to the main strike-slip faults. The parallelogram geometry that results is consistent with structural deformation recorded in the Bristol
Channel region (Rawnsley et al., 1992). The angles of the joints observed in relation to the main faults are characteristic of conjugate shear fractures (Twiss & Moores, 1992) and further supports the occurrence of strike-slip movement. Sinistral slip is indicated by the fault and joint orientations and is consistent with the N-S compression, tectonic stresses and the orientation of the Conwy Valley Fault System.

The orientation of fracture opening, shear (local and regional) and folding is all consistent with the N-S directed compression. High fluid pressures that built up following each fault reactivation and subsequent cement sealing event, resulting in brittle and mixed mode deformation, multiple vein fills and host-rock/cement brecciation, most likely occurred during the Variscan Orogeny.

High angle North-South trending faults occur perpendicular to fold hinges and on fold limbs. They also display striations of varying orientation (vertical, horizontal and oblique) making it difficult to identify the timing of each reactivation. However, the NE-SW faults were reactivated strike-slip movement in addition to normal movement. The architecture of the faults also varies. Fault drag folds are observed immediately adjacent to the fault plane consistent with normal faulting but could also have occurred during strike-slip movement (Mondino, pers. Comms. 2011). Structural orientations, shear indicators and cement are evident at the fracture scale. Across the Great Orme N-S and NE-SW fractures display a close cross-cutting relationship suggesting that although the N-S and NE-SW faulting was coincident, N-S background fracturing was ongoing during the Early Carboniferous. *En echelon* arrays and local shear is observed mainly within N-S oriented fractures. The fractures are vertical and primarily mode 1, open mode. Where the fractures are connected to through-going fractures and faults, they host dolomite cements (D3-D7) in addition to calcite cements. Further analysis is required to determine the exact calcite cement phases, although post-dolomite phases include C10-c19. Moreover, they display multiple opening and cementation events. Toward the top of the Great Orme within the Great Orme, Bishops Quarry and Summit Limestone Formations zebra textures have been observed extending from vertical N-S faults. The zebra textures
appear very similar to those observed within the Pier Dolomite Formation (see previous section) and host D3-D5 cements. This further indicates the NE-SW, NW-SE and N-S fault systems across the Great Orme are connected. In addition, it also suggests that localised overpressures were created along these N-S faults during repeated reactivation and sealing events. A larger scale and more impressive occurrence is seen within the Pier Dolomite Formation where faulting and fluid flow led to laterally extensive zebra textures and veining (Figure 6.7). The laterally extensive zebra textures and veining are located at dolomitised mudstone-dolomite bed boundaries and hosts dolomite cement with floating host-rock dolomite clasts up to 30cm in diameter.

The cements hosted by the N-S, NE-SW and NW-SE faults and fractures include C5-C16, D3-D7 and diagenetically late (post-Variscan) meteoric C17-C19 phases that exploit dissolution enhanced secondary porosity, which cross-cuts the dolomite and earlier calcite phases. D3 cements are primarily located within the Pier Dolomite faults and fractures display saddle textures and crack-seal and bridging textures. These textures indicate cementation during fracturing (Laubach et al., 2010) and repeated fracturing events. In comparison, phases D6-D7 are situated within the fractures connected to faults higher in the stratigraphy, display unit extinction and passive fill textures. These fractures display more limited number of fracturing episodes. The change in orientation (N-S/NE-SW to NW-SE) of the fractures hosting D6-D7 indicates a change in major stress direction and a separate episode of diagenesis. However, further sampling and analysis is required to fully constrain the timing.

Structural diagenetic stages 3 to 4 occurred during Variscan compression. On the Great Orme the folding induced flexural slip along favourable bedding planes and reactivated faults followed by brittle deformation including faulting and fracturing with associated fluid flow. Seismic scale investigations by (Williams & Eaton, 1993) to the north of the Great Orme have identified onlap of younger Jurassic sediment onto Carboniferous carbonates suggesting that the Great Orme was most likely a post-Variscan high.
Structural diagenetic stage 5

Between the end Permian and Cretaceous, North Wales was affected by the regional NW-SE orientated rifting related to the opening of the Atlantic, which resulted in regional, NE-SW trending normal faults (Chadwick & Evans, 1995; Coward et al., 2003). This tectonic period could have potentially reactivated structures on a more local scale (Great Orme) and allowed the downward migration of fluids that influenced the mineralisation of structural diagenetic phase 5. However, there is little evidence of this rifting phase from field and petrographical observations.

Stage 5 is characterised by the development of low angle E-W trending faults as well as mode 1 fractures, and reactivation of earlier fault and fracture systems (Figure 6.10). The faults dip at about 45° and striations, brecciation and fault-related folds indicate a spectrum of normal, reverse and strike-slip motion.

The dominant E-W orientation, perpendicular to bedding and cross-cutting en echelon and zebra textures, indicates a change in principal stress direction from the N-S directed compression that characterised Structural diagenetic stages 3-4. Mode 1 fractures are consistent with an E-W oriented maximum stress direction that resulted in compression and brittle deformation. This is further supported by the reverse movement identified to the south west on the Great Orme. Once again, the low angle reverse deformation displays a mesh network of joints consistent with ‘fault fish’ that formed parallel to the direction of movement. This reactivation of faults and fractures could have occurred during reburial (Triassic-Cretaceous) during a period of regional extension and burial (Floodpage, 2001). Subsequent compression represented by reverse fault movement most likely occurred during Tertiary (Alpine Orogeny) NW-SE and WNW-ESE compression (Coward & Deitrich, 1989; Davies et al., 2004). It is difficult to accurately determine the nature of post-Jurassic deformation as post-Jurassic sediments are absent from onshore North Wales and the adjacent Cardigan Bay Basin (Tucker & Arter, 2003) and Cheshire Basin (Lewis et al., 1992; Smith, 1999). Only in the East Irish Sea Basin have Cretaceous sediments been recorded (Floodpage, 2001). The widespread
absence of these units is considered to be a result of Late Cretaceous-Tertiary (Alpine) NW-SE trending inversion (Lewis et al., 1992; Floodpage, 2001; Tucker & Arter, 2003). This is consistent with the latter phase of fault reactivation and change in principal stress direction observed within the Conwy Valley System (Shackleton, 1953). In the absence of onshore post-Carboniferous strata in North Wales, evidence for subsequent tectonism from surrounding areas (e.g. Jackson et al., 1995) includes reactivated strike-slip (and oblique-slip) structures observed in seismic and classic inversion structures such as folding and exposure surfaces seen within the Bristol Channel area is not observed (Turner, 1997).

The faults and fractures of Structural Diagenetic Stage 5 host calcite cements C15 which include cubic chalcopyrite mineralisation. Following diagenetic alteration there are also a variety of secondary copper minerals such as malachite and azurite (Lewis, 1994, 1996; Ixer & Budd, 1998 and references therein). Minor volumes of dolomite (heavily weathered D6-D7) occur where fractures cross-cut previous fault and fracture sets suggesting minor remobilisation of precursor dolomite cements.

The change in mineralisation and cement composition within stage 5 suggests a significant change in fluid composition, source and/or fluid flow pathways. It has been suggested, on kinematic evidence, that the E-W trending structures that characterise Stage 5 represent post-Variscan deformation associated with re-burial and compression in the Cretaceous-Tertiary. Correspondingly, following dewatering and compression during the Variscan Orogeny, basal and formational fluids would have become depleted (chapters 5 and 7, Juerges et al., in prep). Consequently, it is expected that fluids most likely originated from a different source (e.g. overlying or adjacent Permo-Triassic sediments) during the second mineralisation event. Trace elements responsible for copper mineralisation could have been sourced from detrital siliciclastic minerals, clays and/or volcanic rock (Holmes et al., 1983). This is consistent with the stable isotope data and models for copper mineralisation within Northern England (Holmes et al., 1983). In this sense, the Cu-mineralisation on the North Wales Platform is interpreted to co-date copper deposits to the east (e.g. Alderly Edge, Holmes et al., 1983).
In summary, the NNW-SSE Alpine compression on the Great Orme manifests as low angle faulting, fracturing with associated copper mineralisation characterises structural diagenetic phase 5.

**Structural diagenetic stage 6**
Following Tertiary inversion, the UK was subject to pulses of NE-SW orientated extension and volcanic dyke emplacement (Coward et al., 2003). During this period, North Wales was still a region of emergence with limited tectonic activity (Davies et al., 2004). The final stage (6) consists of barren open fractures that cross-cut all other structural features. They are predominantly evident on the platform margin and remain open. It is suggested that they formed as a result of relaxation following the final uplift event (Figure 6.10). Thus, it is suggested that the barren, open fractures assigned to structural diagenetic stage 6 were a result of relaxation with minimal influence from extension.

**6.8 Conclusions**
The Great Orme presents a complex structural history. Therefore, superposition, cross-cutting relationships and diagenesis has been employed to unravel the structural diagenesis and kinematic evolution.

Six structural diagenetic stages have been identified 1) deposition and extension, 2) subsidence and burial, 3) onset of Variscan compression, 4) main phase of Variscan compression, 5) re-burial and Alpine compression and 6) relaxation.

Detailed field observations presented in this study demonstrate the first stage of deformation comprises early fracturing followed by chemical compaction and stylolite development with increasing burial. Subsequent vertical and sub-vertical veins were emplaced at high pressure during subsidence. During this period normal faults following Caledonian trends were most likely active. The onset of compaction related to the Variscan Orogeny is marked by flexural-slip and shearing occurred along bedding planes. At this time moderate to high fluid pressures resulted in emplacement of bed parallel veins and *en echelon*
veins orientated normal and sub-parallel to bedding. As compaction and folding of the Great Orme succession developed, areas of brittle deformation and localised overpressure occurred with associated brecciation of host rock and vein fill. The dominant N-S and NE-SW fractures hosting dolomite are evident across the Great Orme and zebra vein textures were produced primarily within the Pier Dolomite Formation and close to vertical faults within the other formations. Normal faults were reactivated with a component of shear, superimposing sub-horizontal slickensides onto vertical kinematic textures. Large scale NE-SW trending strike-slip faults indicate multiple reactivations and hosts dolomite cement, brecciated dolomitised host rock limestone and younger calcite cements.

The subsequent set of veins and fractures display a change in the direction of principal stress responsible for veins that cross-cut all earlier sets. In addition, there is a distinct change in fracture fill (copper and calcite) suggesting a change in fluid source and/or flow pathways. This event further reactivated earlier normal and strike-slip faults resulting in brecciation, leaching and mineral emplacement. The exact timing of the copper mineralisation is unknown. However, potential sources of the fluid and trace elements and the drive for fluid migration most likely occurred during re-burial and the second uplift event during the Late Jurassic to Early Tertiary. The final structural diagenetic stage (6) occurred following exhumation of the Great Orme and North Wales Platform. The uplift and folded areas most likely underwent relaxation resulting in barren open fractures (E-W and NW-SE) that cross-cut all previous structural and diagenetic features.

The results of this study have demonstrated that multiple reactivations of structures can result in a complex structural and fluid flow history. Observations of structural features alone provide a limited understanding of the kinematic evolution. In order to better constrain structural evolution, combining structural analysis with diagenetic study at a range of scales is imperative. However, there is potential for misinterpretation arising from biased sampling or limited data and observations. It is suggested from this study that combining structural and diagenetic observation is useful where the structural history is relatively simple and discrete phases of cementation can
be determined petrographically and geochemically. On-going diagenetic processes and over-printing can further complicate matters by destroying evidence for the process of formation of prior diagenetic events. In addition, inherited geochemistry can result in similar petrographic characteristics for different events and mask the signal of the fluid source, thus caution is urged when employing the combined methodologies.

Acknowledgements
The authors would like to gratefully acknowledge NERC and Shell International, Rijswijk for funding this PhD research, grant NE/G523712/1. The Countryside Council of Wales (CCW), Great Orme National Park and the managers of the Great Orme Mines are thanked for access and permission to sample. Jonathan Wood and Myron Thomas (University of Manchester) are thanked for field assistance.

Figures

Fig.6.1. Regional map showing the study area, Great Orme Wales Platform, position of the East Irish Sea Basin and their relationship to major structural features (Modified from Warren et al., 1984; Jackson et al., 1993).
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arrays; Yellow dotted lines = Bed contacts, Black dotted lines = margin of geobody, large black arrows indicate the direction of movement, B: breccia, BP: bed plane, Bp.E: bed-parallel en-echelon, D: dolomite, Lmst: limestone, Sty: stylolite
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planes; Yellow dotted lines = Bed contacts, Black dotted lines = margin of geobody, large black arrows indicate the direction of movement, B: breccia, BP: bed plane, Bp.E: bed-parallel en-echelon, D: dolomite, Lmst: limestone, Sty: stylolite
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## Tables

### Table 1. Summary of paragenesis, petrographic characteristics and stable isotope ranges

<table>
<thead>
<tr>
<th>Cement</th>
<th>Morphology</th>
<th>CL</th>
<th>Plane light</th>
<th>$\delta^{18}$O (‰ VPDB)</th>
<th>$\delta^{13}$C (‰ VPDB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D0</td>
<td>Mmimetic</td>
<td>Medium pink/ red</td>
<td>Limpid, unit extinction</td>
<td>-6.64</td>
<td>1.35</td>
</tr>
<tr>
<td>D1</td>
<td>Planar-s</td>
<td>Medium pink/ red</td>
<td>Limpid, unit extinction</td>
<td>-6.64</td>
<td>1.35</td>
</tr>
<tr>
<td>D2</td>
<td>Planar-e</td>
<td>Medium pink/ red</td>
<td>Turbid, unit extinction</td>
<td>-6.64</td>
<td>1.35</td>
</tr>
<tr>
<td>D3</td>
<td>Planar-e, baroque</td>
<td>Medium pink/ red</td>
<td>Limpid, sweeping extinction</td>
<td>-6.93</td>
<td>2.96</td>
</tr>
<tr>
<td>D4</td>
<td>Baroque</td>
<td>Red</td>
<td>Limpid-turbid, sweeping extinction</td>
<td>-6.31</td>
<td>1.62</td>
</tr>
<tr>
<td>D5</td>
<td>Xenotopic</td>
<td>Red</td>
<td>Limpid-turbid, sweeping extinction</td>
<td>-6.31</td>
<td>1.62</td>
</tr>
<tr>
<td>D6</td>
<td>Planar-s, baroque</td>
<td>Dark red-brown</td>
<td>Turbid, unit extinction</td>
<td>-5.80</td>
<td>0.12</td>
</tr>
<tr>
<td>D7</td>
<td>Xenotopic, diffuse</td>
<td>Bright pink</td>
<td>Turbid, unit extinction</td>
<td>-5.80</td>
<td>0.12</td>
</tr>
</tbody>
</table>

*Table 1. Summary of paragenesis, petrographic characteristics and stable isotope ranges*

### Table 2. Summary of fault/ fractures across the Great Orme

<table>
<thead>
<tr>
<th>Set</th>
<th>Orientation</th>
<th>Cement, Phase</th>
<th>Mineralisation</th>
<th>Kinematic mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N-S</td>
<td>Dolomite, C5-C13, D3</td>
<td>Cu-Fe-Pb-Zn</td>
<td>Opening + mixed</td>
</tr>
<tr>
<td></td>
<td>NNW-SSE</td>
<td>Dolomite D3</td>
<td>-</td>
<td>Opening + mixed</td>
</tr>
<tr>
<td></td>
<td>NNE-SSW</td>
<td>Dolomite D3</td>
<td>-</td>
<td>Opening + mixed</td>
</tr>
<tr>
<td>2</td>
<td>E-W</td>
<td>Calcite, dolomite C12+, D6, D7</td>
<td>-</td>
<td>Opening</td>
</tr>
<tr>
<td>3</td>
<td>NW-SE</td>
<td>Calcite and dolomite C5-C13, D3, D6, D7</td>
<td>Pb-Zn</td>
<td>Opening + mixed</td>
</tr>
<tr>
<td>4</td>
<td>NE-SW</td>
<td>Calcite C5-C13</td>
<td>-</td>
<td>Opening</td>
</tr>
</tbody>
</table>

*Table 2. Summary of fault/ fractures across the Great Orme*
Chapter 7: Geochemical fingerprinting of a complex dolomite body, Lower Carboniferous North Wales Platform, UK
7.0 Geochemical fingerprinting of a complex dolomite body, Lower Carboniferous North Wales Platform, UK

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Keywords: Strontium; Dolomite; Dinantian; North Wales Platform

Abstract

Dolomitised limestone bodies located on the margin of the Lower Carboniferous North Wales carbonate platform display a complex paragenesis and close relationship with areas of structural deformation. Focusing on a small headland outcrop (the Great Orme), eight phases of dolomite (D0-7) have been identified from detailed field and petrographic observation, stable isotope (δ¹⁸O/δ¹³C) techniques and element analysis. The paragenesis demonstrates progressive porosity destruction and overprinting by consecutive matrix replacive and fracture controlled cementation during burial. However, overprinting and elemental/isotopic remobilisation during successive fluid flow events has masked the original geochemical composition, making determination of fluid source and timing problematic using conventional geochemical techniques alone. Therefore an integrated structural, sedimentological and geochemical approach has been employed. Strontium (⁸⁷Sr/⁸⁶Sr) isotopes and rare earth elements plus Yttrium (REE + Y) analyses have been applied to
these Lower Carboniferous hosted dolomites in order to robustly characterise and fingerprint the source and timing of isolated dolomite phases.

Limestone matrix replacement by dolomite (D0 to D2) occurred early in the diagenetic history as a result of circulation of Mg-saturated fluids through shoaling facies on the North Wales Platform margin. Subsequent fault and fracture controlled phases, D3 to D7, were emplaced during dewatering of the basin, initially via compaction and then by dolomitising fluids expelled during the onset of Variscan compression. REE + Y data displays similar patterns for all samples analysed and suggest dolomitisation and dolomite cementation took place from modified marine porewaters. A negative Ce anomaly, suggestive of a marine signature, is present within the early dolomite phases (D0 to D3) and diminishes with successive phases (D4 to D7). Light rare earth elements (LREE’s) display a depletion, which has been attributed to the re-mobilisation of carbonate (dolomite) and recrystallisation. The results of the strontium isotopic analysis are consistent with diagenetic modification during early burial from seawater-derived fluids. An increase in radiogenic signature with successive dolomite phases suggests a contribution from a basinal fluid source. These findings are consistent with data acquired through standard techniques; petrographic, trace element and stable isotope analysis. In addition, the data presented indicates that the composition of the host-rock carbonate strongly controlled the distribution and composition of successive diagenetic phases.

This study provides important physio-chemical information on the environment and timing of dolomitisation and the source of the fluids for a small, but structurally and diagenetically complex dolomite body. The data can help provide a framework for understanding and predicting the distribution of fault/fracture controlled dolomite bodies, which is of great interest academically and within the petroleum industry.
7.1 Introduction
Fault and fracture controlled dolomitisation has been widely described within a number of Lower Carboniferous platform limestones throughout the UK and Ireland (Haggerty & Bottrell, 1997; Hollis & Walkden, 2012). The deposits display varying petrographic and geochemical characteristics but similar timing and models of emplacement (see Pattrick & Russell, 1989; Haggerty & Bottrell, 1997; Gawthorpe, 1987; Shelton et al., 2011; Hollis & Walkden, 2012 and references therein). Whilst many of these dolomite deposits have received extensive study, selective dolomitisation on the North Wales Platform has received little attention to date.

In recent years there has been increasing interest in fault-related dolomite bodies, which has been driven by mineral exploration and hydrocarbon exploration and production (Braithwaite et al., 2004; Davies & Smith, 2006; Wilson et al., 2007). A number of field and petrographic studies have documented an intimate relationship between dolomitisation and structural deformation, where faults and fractures are considered to be effective flow pathways for dolomitising fluids (Duggan, 2001). However, still relatively few fault-related dolomite bodies have been described in detail (e.g. Davies & Smith, 2006; Wilson et al., 2007; Lopez-Horgue, 2010; Sharp et al., 2010) and the origin and controls on these dolomites has been an area of much debate (Machel, 2004). Mechanisms invoked to explain the origin and distribution of fault-related dolomitisation have focused on geothermal convection of seawater and expulsion of hydrothermal basinal fluids (Morrow, 1998; Machel, 2004; Whitaker et al., 2004; Wilson et al., 2007). Constraints on many of these mechanisms include fluid salinity, volume and flow rates (Machel, 2004). There are also relatively few descriptions of the distribution of fault/fracture controlled dolomitisation. In general, fault related dolomitisation can result in both stratabound and non stratabound dolomite bodies, the distribution of which is driven primarily by the available permeability and reactive surface areas (Whitaker & Xiao, 2010). Moreover, dolomitisation can have complex emplacement histories and often display overprinting of
successive phases, such that robust geochemistry can help to conceptually reconstruct fluid flow by fingerprinting isolated cement phases (e.g. Banner, 2005). Standard techniques such as stable isotope and trace element analysis provide the basis to characterise these isolated cement phases and give an indication of the composition of the fluids and chemical reactions responsible for diagenetic products. However, where fluid-rock interaction has been extensive, these techniques alone may not enable a clearly defined paragenesis. The use of rare earth elements (REE) and strontium isotopes is becoming more prevalent in diagenetic studies as they have been recognised as an important source of information regarding the physio-chemical conditions during the precipitation of dolomite (Banner et al., 1988; Bau & Moller, 1992; Kucera et al., 2009). In particular, REE analysis has proved useful in determining the origin of dolomitising fluids (Qing & Mountjoy, 1994; Johannesson et al., 1996; Kucera et al., 2009). Rare earth elements in seawater are most commonly derived from the upper-crust and their incorporation is controlled by redox reactions, fractionation and temperature-controlled partitioning, competition, fluid composition and bio/diagenetic influences (McLennan, 1994). Potential sources of the REE’s include marine water, basinal sediments and leached host-rock carbonate and siliciclastics encountered by the fluid during migration (Banner et al., 1988; Elderfield et al., 1990; Johannesson & Lyons, 1995; Johannesson et al., 1996). REE analysis is often utilised during diagenetic studies in order to better constrain the fluid source(s) for precipitation as REE’s are relatively stable and are therefore considered to represent the composition of the precipitating fluid. Modification of REE concentrations occurs during alteration under increased temperatures and high water:rock ratios during diagenesis (Banner et al., 1988). Therefore, at low temperatures (<60°C) modification of the REE concentration of the fluid, by fluid-rock interaction, requires water-rock ratios of ≥10^5 (op. Cit.; McLennan, 1994). Furthermore, the abundance, fractionation and anomalies within the REE profile indicate the mode of
crystallisation and the physio-chemical environments which the fluids encountered (Bau & Moller, 1991).

Strontium ($^{87}\text{Sr}/^{86}\text{Sr}$) isotope analysis is an increasingly utilised technique within diagenetic studies that is complementary to standard techniques and REE analysis. A number of studies (e.g. Swart et al., 1987; Mountjoy et al., 1992; Hoefs, 2009; Banner, 2004) demonstrate that Sr isotope analysis can provide important information regarding the mineralogy, salinity, fluid source and fluid rock interaction (Banner, 1995). The key to the relative success of the technique is the variability in concentration within different Sr sources, lack of partitioning as a result of crystallisation and the link to trace element partitioning (op. Cit.).

7.2 Geological setting

The North Wales Platform developed within a back-arc extension regime during the Lower Carboniferous (Dinantian) (Davies et al., 2004). During this time the resulting structural topography, sub-tropical climate and a dearth of siliciclastic input produced favourable conditions for carbonate production and the evolution of ramp to rimmed platform geometries on the footwall highs of fault blocks (Somerville et al., 1989; Adams et al., 1990). Dinantian carbonate sediments mainly consist of packstones to grainstones, which are characteristic of the platform margin and subtidal depositional environments (Bancroft, 1986; Somerville et al., 1989; Juerges et al., in prep, chapter 5) (Figure 7.1). Late Dinantian sedimentation comprised deeper water micritic sediments following a marine transgression (Davies et al., 2004).

Carbonate production ceased in the area at the end of the Brigantian due to the onset of Variscan uplift and siliciclastic sedimentation. From the Namurian onwards, deposition of basinal mudstones and fluvio-deltaic deposits prevailed (Jerrett & Hampson, 2007). During the Late Carboniferous and Early Permian the platform was subject to Variscan tectonism resulting in regional and local scale NE-SW to ENE-WSW orientated folding, N-S and NE-SW faulting and reactivation of normal and strike-slip Caledonian basements faults (Nichols, 1968; Lee et al.,
1990; Williams & Eaton, 1993). From the Late Permian to the Cretaceous the region was subject to thermal relaxation, subsidence and a period of NW-SE oriented extension related to opening of the Atlantic (Chadwick & Evans, 1995; Coward et al., 2003). By the Late Cretaceous, the North Wales Platform was subject to a second uplift event related to NW-SE trending Tertiary (Alpine) compression (Lewis et al., 1992; Floodpage, 2001; Tucker & Arter, 2003). This resulted in reactivation of earlier fault/fracture networks, the development of low angle E-W trending faults and emplacement of copper mineralisation (Juerges et al., in prep, chapter 6).

Due to the nature of the outcrop and lack of post-Brigantian sediment at the present day, it is difficult to constrain the amount of sedimentation that occurred on the platform and therefore the amount of sediment removed due to uplift and erosion. However, data from Williams & Eaton (1993, pg. 493, Figure 5) displays onlap of Triassic sediment onto the Dinantian platform carbonates indicating removal or absence of Late Carboniferous sediments. Burial history curves constructed for NE Wales have inferred burial depths of up to 1.5km (Al-Fadel, 1985).

**Distribution of dolomitisation**

Dolomitisation on the North Wales Platform occurs in small pockets of up to 8km² along the palaeo-platform margin, adjacent to the East Irish Sea and Pennine Basins, and displays a close spatial and temporal relationship with areas of structural deformation. The dolomite bodies, and their relationship with faulting and fracturing potentially provide important information about the tectonic development of the East Irish Sea basin and the North and Wales Platform, fluid source, and flow pathways during Carboniferous and post-Carboniferous basin evolution. This study focuses on the Great Orme, a headland on the North Wales coast that hosts the largest dolomite body on the North Wales Platform. The paragenetic sequence of the Great Orme has been described in the context of the tectono-stratigraphic evolution of the North Wales Platform in Juerges et al., (in prep, chapters 5 and 6). In this paper we present complementary REE and strontium isotope data in order to specifically
fingerprint the individual dolomite phases and determine a) evidence for the role of seawater in dolomitisation and b) assess the extent of fluid/rock interaction between the dolomitising fluids and the host limestone, underlying Lower Palaeozoic basement and/or siliciclastic units within the East Irish Sea Basin.

Earlier models of dolomitisation on the Great Orme have invoked fluid expulsion during the waning phases of basin dewatering following MVT mineralisation (Ixer & Stanley, 1996). However, recent field and petrographic work (Juerges et al., in prep, chapter 6) indicate that dolomitisation occurred prior to the main stage of Variscan (MVT) mineralisation and was related to reactivation of fault and fracture networks with a strike-slip component. Through combined field, petrographic, REE and isotope (C, O, Sr) data, this study aims to further characterise and constrain fluid source and controls on the distribution of the dolomite. Moreover, the data presented in this paper will be assessed in light of the updated tectono-stratigraphic framework for the North Wales Platform (op. Cit.).

7.3 Study location

The Great Orme is an 8km² headland on the north coast of Wales, UK and is comprised of 200 meters of well exposed Asbian and Brigantian strata. Full details are given in geological sheet 94 and the corresponding memoir by Warren et al. (1984) (see also Juerges et al., in prep, chapter 5). The Great Orme succession comprises six distinct units including the Pier Dolomite Formation, Tollhouse Mudstone Formation, Great Orme Limestone Formation, Craig Rofft Sandstone Member, Bishops Quarry Limestone and Summit Limestone Formations (Figure 7.2). The outcrop represents part of the northern margin of the North Wales Platform which is characterised by well bedded, platform margin and platform top facies. Five depositional domains have been identified: platform margin, deep subtidal, shallow subtidal, restricted lagoon and emergent that record an overall transgressive succession containing subordinate transgressive-regressive cycles (Juerges et al., in prep, chapter 5). The platform margin
environment is characterised by knoll reefs and high energy shoals consisting of crinoidal and coral debris equivalent to units observed in the east of the study area around Prestatyn (e.g. Bancroft, 1986; Somerville *et al.*, 1989; Davies *et al.*, 2004). The sheltered deep subtidal environment is characterised by alternating beds of mudstone and calcareous siltstone (wacke-packstone) that constitute the Tollhouse Mudstone Fm and the base of the Great Orme Limestone Fm. The shallow subtidal to restricted lagoonal environment is dominated by shallowing-upward successions that are terminated by minor exposure surfaces and incursions of fine grained sandstone. The shallow subtidal (peritidal) to deep subtidal deposits at the summit of the Great Orme comprises wackestones and packstones with brachiopod (*Gigantoproductid*) rich horizons as seen in the Bishops Quarry and Summit Limestones (Warren *et al.*, 1984; Juerges *et al.*, In prep, chapter 5).

This study focuses on the dolomitised limestone that is exposed on the Great Orme, and which is mainly concentrated at the base of the succession replacing Asbian limestone host-rock and forming the Pier Dolomite Formation (Warren *et al.*, 1984; Oldham, 1987; Lewis, 1996; Ixer & Stanley, 1996). Dolomite within stratigraphically higher units is only observed within fractures and in close proximity to faults (Lewis, 1996, Juerges *et al.*, in prep, chapters 5 and 6). The Great Orme exhibits a complex diagenetic history that records the evolution of porosity and permeability through pervasive early cementation and dolomitisation within the marine to shallow burial realms followed by fault/fracture controlled diagenesis in the deep burial and telogenetic realms (see also Juerges *et al.*, in prep, chapters 5 and 6). Four early diagenetic calcite cement phases dominate the Asbian and Brigantian units; three syntaxial calcite cements (SC1-SC3) and passive void fill C4. The syntaxial cements are most extensively developed within crinoidal grainstone facies, whereas C4 fills any remaining interparticular porosity. These early calcite phases occlude the majority of primary and early dissolution enhanced porosity. As a result, successive diagenetic phases are
primarily controlled by secondary fracture porosity (Juerges et al., in prep, chapter 5). Shallow to deep burial diagenesis is characterised by dolomite (matrix replacive and vein cement), burial calcite, mineralisation (Mississippi Valley-type and copper) and subsequent telogenetic (meteoric) calcite cements precipitated following uplift of the North Wales Platform (op. Cit.).

7.4 Methodology
Dolomite and whole rock samples were collected from natural outcrop and disused quarries and mines. Samples were chosen with respect to vein orientation, position relative to faults, facies and stratigraphic position. Polished sections were prepared for 45 samples from five localities around the Great Orme. Polished sections were half stained with Alizarin Red S and Potassium Ferrocyanide following Dickson (1965). Isotope and geochemical analyses were conducted on all samples. The samples form part of a wider dataset from across the North Wales Platform (see chapter 5, Appendix 10).

Petrographic analysis
Basic petrographic observations were carried out using plane light and cathodoluminescence (CL). 25µm thick polished sections were examined in order to identify isolated cement zones based on texture and carbonate staining and further determine the cross-cutting relationships between diagenetic features. Photomicrographs of the polished sections were acquired using a Progres C10 Laser Optik System and a Cambridge CCL Cold Luminoscope 8200 mk3, operated at an accelerating voltage of 10Kv, a vacuum of 2 Torr and gun current of 300Kv.

Major and trace element analysis
In situ Major and trace element analysis was carried out using ICP-AES, electron microprobe and TOFSIMs ion microprobe. The analysed elements include Fe, Mg, Mn, Ca, Sr, Al. Further, analysed elements (Cu, Pb, Zn, Na and Rb) were selected because of their association with
mineralisation and with burial including cementation. ICP analysis was conducted using 100mg of powdered samples of host rock limestone and isolated dolomite phases. Powdered samples were treated with 6M HCl for 24 hours to digest the carbonate phases. An aliquot containing 10 ml of solution was then transferred to an ICP vial. Corresponding samples were drilled from hand specimens and their purity checked where necessary by XRD techniques. Trace element concentrations were measured using a Perkin-Elmer Optima 5300 dual view ICP-AES with reproducibility of 0.1‰ (1σ).

Electron microprobe and Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) analysis were carried out using 25µm, unstained polished sections, which were carbon coated prior to analysis. Trace element concentrations were measured using a Cameca SX 100 Electron Microprobe. Operating conditions: accelerating voltage of 15Kv, beam current of 20nA, beam size of 5µm or 10µm and internal standards were used for calibration. TOF-SIMS was conducted using the method of King (2009) and was operated using a gold beam, emitting Au+ ions, ~1nA direct current, 25keV focused to a <1micrometer spot. The beam was operating with ~20ns pulses that rastered across the sample. Mass resolution was ~3000 mass resolving power. Total secondary ion maps of the analysed area were used to define areas for detailed study. Mass resolved images and quantitative elemental abundances were then obtained.

Stable isotope analysis
Stable isotope-analysis was conducted at the University of Liverpool. Powdered samples of host rock and discrete cement phases were acquired using a tungsten-tipped precision drill. Samples of calcite were reacted (to completion) with phosphoric acid under vacuum, at temperatures of 25 °C (McCrea, 1950). Gases were measured by dual-inlet, stable isotope ratio mass spectrometry using a VG SIRA10 mass spectrometer. Isotope ratios were corrected for $^{17}$O effects following the procedures of Craig (1957). Oxygen isotope data were adjusted for
isotopic fractionation associated with the calcite-phosphoric acid reaction using a fractionation factor (α) of 1.01025 (Friedman & O’Neil, 1977). Samples were run against an internal standard and all results were reproducible to ±0.1‰ (2σ). All data is reported relative to the VPDB standard.

**Rare Earth Element analysis**

Powdered samples of host-rock limestone, bulk dolomite and individual cement zones were digested in 2ml of 20% HCl before dilution to 2% HCl. In addition, two blank samples were prepared in the same way for reproducibility. Corresponding samples were drilled from hand specimens and their purity checked where necessary by XRD techniques. REE’S and Y concentrations were measured using ICP-MS with an Agilent 7500cx mass spectrometer. Samples were run against internal standards and reproducibility of 0.1‰ (1σ). All samples are reported in mg/l or ug/l (ppm or ppb respectively).

**Strontium Isotope analysis**

Sampling and Sr isotope analysis was carried out at the NERC Isotope Geoscience Laboratory (NIGL) in Keyworth, Nottingham. Powdered whole rock and discrete dolomite cements were obtained using a tungsten-tipped micro-mill following the methodology of Charlier et al. (2006) and Pollington & Baxter (2011). Sample purity was checked where necessary by XRD. Sr (Oak Ridge $^{84}$Sr, 1.1593ppm) and Rb spikes were added to each sample to boost the signal. Strontium was extracted from the rock powders for isotopic analysis using Sr Spec extraction chromatographic resin. Column preparation and chemical separation were conducted following the methodology of Deniel & Pin (2001) and Charlier et al. (2006). Prior to analysis the Sr samples were mixed with Tantalum (Ta) emitter solution, loaded on to single Rhenium (Re) filaments and subjected to a 2A current. Sr isotope ratios were measured on the NIGL Thermo-Finnigan Triton TIMS instrument in static collection mode. An internal NBS 987 standard was used for
calibration with a reproducibility of +0.1%0 (2σ). During TIMS analysis spiked samples were run in the same fashion as unspiked samples. However, the results of spiked samples had to be corrected, off-line, for spike contribution using standard techniques (op. Cit.). All results are reported to the NBS 987 standard.

7.5 Results

Brachiopod sample
Two unaltered brachiopod samples, as determined by petrographic analysis and XRD, were selected for elemental and isotopic analysis in order to provide a comparative ‘original seawater’ signature. For full details see Table 7.3, 7.4. REE results display classic seawater trends with a ‘flat roof’ whereby the MREE and HREE’s display little variation and a large negative Ce anomaly is observed (Nance & Taylor, 1976; McLennan, 1994), with total REE concentrations of 0.041564 ug/l. Brachiopod samples display an average Sr isotope ratio of 0.707485.

Dolomite paragenesis
Several dolomite phases have been identified petrographically (D1-D7) (Table 7.1, 7.2). These phases occur as matrix replacement and vein fill dolomite. Early matrix replacement D1 and D2 are volumetrically the most important phases on the Great Orme and are readily identifiable in outcrop by their distinctive toffee brown colour. Later vein cements (D3-D5) range from rusty brown to colourless in outcrop and are observed within all stratigraphic units. The veins sampled range in thickness from 0.5-3cm and strike N-S and NE-SW.

D0-D2

Distribution
D0 to D2 are volumetrically the most important phases on the Great Orme and comprise the majority of the Pier Dolomite Formation. They pervasively replace Asbian Limestone at the base of the Great Orme (8km², ~140m in height). Determination of the true lateral extent of the
dolomite is constrained by the size of the outcrop, although dolomite terminations are visible along the NE part of the beach. The terminations are present as sharp boundaries within wackestone-packstone facies such that undolomitised limestone beds are present within the Pier Dolomite Formation. Vertically, the Pier Dolomite Formation terminates against the Tollhouse Mudstone Formation. Moreover, the abundance of D0 to D2 and increased fabric destruction is observed below mudstone beds and shale partings.

_Petrography_

D0 mimetically replaces precursor high magnesium bioclasts (crinoid and echinoid). Crystals are up to 2cm, display euhedral terminations, contain micro-fluid inclusions and display unit extinctions. CL reveals red luminescence with no zoning. D0 is only observed within the Pier Dolomite Fm on the Great Orme. The key localities include the beach, south-east Great Orme and outcrop proximal to the south-west tollhouse. D0 represents a very minor dolomite phase (<1% rock volume).

_D1_ is volumetrically the most important dolomite phase. It occurs as a replacive, pervasive, xenotopic to euhedral, polycrystalline and interlocking mosaic. Crystal sizes range between 50 µm and 2000µm. D1 appears toffee brown with micro-inclusions of fluid and iron oxides concentrated at the crystal margins. Secondary, solid and fluid, inclusions preserve the primary limestone fabric as ghost structures. D1 also occasionally mimetically replaces grains of high Mg calcite, such as crinoids and echinoid fragments. CL reveals variegated, bright pink-red luminescence with bright pink luminescent outer zones on crystals adjacent to vugs.

D2 displays rhombic, well developed crystals, 50 – 250 µm in size. Crystals appear medium dark brown, turbid, inclusion rich and display unit extinction. D2 appears to overprint D1 and is observed in close proximity to fractures (up to 20cm). CL reveals homogenous pink-red luminescence indistinguishable from D1.
The dolomite textures observed within phases D0 to D2, the unit extinction and preservation of fabric suggest that the precipitation took place from low temperature fluids. In addition, D0 to D2 are cross-cut by bed-parallel stylolites indicating replacement occurred prior to pressure solution, interpreted to begin at burial depths of 300m (Sibley & Gregg, 1987).

**Geochemistry and isotope results**

Phases D0 to D2 were distinguished based on their petrographic textures and cross-cutting relationships as seen in plane light and CL. The phases were then characterised using a combination of trace element and isotope (O, C and Sr) geochemistry. Concentrations of Mg, Fe, and Sr remain extremely low 281.96, 14, 32 ppm and may require further analyses to ensure robust data above the detection limit (Table 7.5). These low concentrations are evident from the carbonate staining, which indicates non-ferroan dolomite, and also the moderate to poor luminescence (Figure 7.3). Stable isotopes range from $\delta^{13}$C = 0.8 to 2.3‰ and from $\delta^{18}$O = -5.5 to -7.5‰ (Table 7.3). Results of REE + Y and Sr isotope analysis are shown in Figure 7.5. Total REE concentrations range from 0.246316 to 5.654529 ug/l. REE patterns are similar for all samples analysed but can be separated by subtle variations. REE patterns for D0 and D1 display a relatively large negative Ce anomaly, MREE ‘bulge’ and HREE enrichment relative to the LREE’s but a depletion relative to the MREE’s. In comparison, D1-D2 samples display a more irregular pattern and less variation between LREE’s, MREE’s and HREE’s and as a result the overall REE pattern is not dissimilar to the seawater pattern of the analysed brachiopod sample (Figure 7.5). A Sr isotope ratio of 0.709042 was measured for D1. In a sample where phase separation was not possible, D1-D2 displays an average Sr isotope ratio of 0.709013 (Figure 7.5a).

**D3**

*Distribution*
D3 is observed within N-S and NE-SW orientated faults and fractures throughout the Great Orme but is more abundant within the Pier Dolomite Formation. In addition, D3 is observed in zebra textures, *en echelon* veins and faults, cementing dolomitisated host-rock breccia. The zebra textures comprise alternating bands (up to 2mm thick) of opaque white crystalline and buff coloured matrix replacive and pore-filling dolomite (D3). The veins extend for up to 1m from faults, fractures and bed planes, are between bed-parallel and 20° from bed parallel and are arranged in a planar, stacked pattern or *en echelon* arrays. The zebra textures extend laterally for up to 1m and 30cm in height with rock bridges visible between discontinuous zones of zebra textures. The dolomite cements hosted within the zebra textures display coarse saddle crystals, which are also evident in N-S, NE-SW and bed parallel fracture systems across the Great Orme (Juerges et al., in prep, chapter 6).

**Petrography**

*D3* cements veins and fractures and partially overprints D0-D2 host rock. D3 displays subhedral to euhedral coarsely crystalline saddle dolomite crystals, producing an interlocking mosaic with featherlike and/or rhombic terminations in veins and vugs. Micro-fractures also display bridging textures whereby D3 crystals have precipitated across the width of the fracture and resulted in partial occlusion (Juerges et al., in prep, chapter 6). Crystal sizes range between 500 and 2000 µm, appear grey brown due to micro-inclusions and exhibit sweeping extinction. CL reveals moderate to dull maroon luminescence with a bright luminescent orange subzone in the crystals outer margins. D3 saddle morphologies, with curved crystal boundaries, suggest precipitation from fluids with elevated temperatures, >60°C (Radke & Mathis, 1980). D3 precipitated in extensional fractures that cross-cut and are cross-cut by stylolites. This suggests that the precipitation of D3 began post-lithification and prior to pressure solution during compaction.

**Geochemistry and isotope results**
Trace-element concentrations (Mg, Fe, Sr, Mn) 131.7213, 9.924364, 12.44626, 2403.323 ppm generally remain low in D3 dolomite (Table 7.5). These low concentrations are also evident from the carbonate staining displaying non-ferroan dolomite and also the moderate to poor luminescence (Figure 7.3). Stable isotope values of $\delta^{13}C = 3.0\ %$ and $\delta^{18}O = -6.9\ %$ are recorded (Table 7.3). Total REE concentrations range from 0.886253 to 3.074737 ug/l. D3 REE patterns display a relatively large negative Ce anomaly, a minor positive Eu anomaly and HREE enrichment relative to the LREE’s. Compared to phases D1-D2, D3 samples display a much less pronounced MREE bulge. The negative Ce anomaly is also greatly reduced within samples that display overprinting of multiple dolomite phases (Figure 7.3, 7.5). Sample THM 5 displays a relative depletion in HREE’s and enrichment in LREE’s, which varies from the trends visible for all other samples. D3 display Sr isotope ratios of 0.70901 (Table 7.6a).

**D4-D5**

*Distribution*

Phases D4 to D5 are observed as fracture-fill cements within the Pier Dolomite Formation. The phases succeed D3 cements within fractures and a very minor volume nucleate on crinoid fragments following minor etching.

*Petrography*

*D4* occurs subsequent to etching of D1-D2 and presents as a late syntaxial cement around crinoid fragments. Where D4 occurs within veins, it follows etching of D3 (see Figure. 7.3). D4 is turbid and brown with concentric zones of inclusions (solid and liquid). Crystals range in size from 200 µm to 500 µm and display rhombic terminations. CL reveals a maroon and moderately luminescent cement, faint subzonation and a slightly brighter outer zone which is etched at the margin.

*D5* is heavily weathered and observed exclusively as a vein fill. Rhombic, turbid crystals range in size, up to 500 µm and have a sweeping
extinction. Crystals are often etched and replaced by calcite or quartz. CL is typically very dark red and poorly luminescent with some faint zonation where crystals have undergone differential weathering. 

*D5b* is intergrown with vug fill calcite, and displays moderate relief, rhombic crystals with unit to sweeping extinction. Crystals range in size from 100 µm to 300 µm. CL reveals pink luminescence at the outer zones of the crystals.

D4 to D5 succeed D3 within extensional fractures and display course saddle morphology suggesting elevated fluid temperatures were maintained during precipitation of these phases. Minor zonation and etching at crystal boundaries indicates slight disequilibrium between the precipitating fluids and the previous dolomite phases.

**Geochemistry and isotope results**

Overall, trace element concentrations remain low for Mg, Fe, Sr and Mn (127.4054, 25.85914, 38.31049, 8235.166 ppm; Table 7.5). However, Fe concentrations are elevated compared to the other dolomite phases. These variations in concentrations are evident from the absence of ferroan staining and moderate to poor luminescence, which may have been quenched by the slightly elevated Fe concentration (Figure 7.3). Stable isotopes range from δ¹³C= 1.2 to 1.6 ‰ and δ¹⁸O= -5.4 to -6.6 ‰ (Table 7.3). Total REE concentrations range from 1.797027 to 25.29514 ug/l. D4-D5 REE patterns display a small negative Ce anomaly, a very minor positive Eu anomaly, MREE ‘bulge’ and HREE enrichment relative to the LREE’s but a depletion relative to the MREE’s (Table 5). Samples analysed from two different localities display different trends (Figure 7.5). D4-D5 display average Sr isotope ratios of 0.709409 (Figure 7.6a).

**D6-D7**

*Distribution*

Phases D6 to D7 are observed within N-S, NE-SW and NW-SE fractures that dissect the Great Orme Limestone, Bishops Quarry and Summit Formations.
**Petrography**

*D6* is a fracture controlled cement that also forms replacive halos around the fractures of up to 0.5cm wide, it is inclusion rich, with euhedral and rhombic termination, unit extinction and are medium brown in plane light and outcrop. *D6* appears to preferentially replace the adjacent micritic matrix and partially micritised grains. It also occasionally replaces *C2* calcite, which occludes moulds and vug (e.g. sample 767.8, grid ref 7670 825). In CL, *D6* displays a weak, dark pink-red luminescence.

*D7* Heavily weathered *D7* cross-cuts and occasionally syntaxially overgrows *D6*. Crystals are turbid and contain abundant micro-inclusions to give a powdery brown colour in PPL. Crystals range in size from 50 µm to 200 µm. CL reveals bright pink luminescence, followed by medium bright pink luminescence, little zonation is observed. *D6* to *D7* are comprised of blocky and massive fracture fill, with unit extinction.

**Geochemistry and isotope results**

Overall trace element concentrations remain low for Fe (avg. 0.087-25.85 ppm), Mg (avg. 1.59-295.98ppm) and Sr (avg. 0.48-38.31 ppm) (Table 7.5). Phases *D6-D7* display increased Mn concentrations compared to earlier dolomite phases and a relative increase from *D6* to *D7*. This increase in Mn is evident from the moderate to bright pink luminescence revealed by CL (Figure 7.3). Stable isotopes range from $\delta^{13}C = -0.4$ to 1.2 $\%_o$ and $\delta^{18}O = -5.6$ to -6.1 $\%_o$ (Table 7.3). Total REE concentrations range from 1.370186 to 3.81457 ug/l, which is elevated compared to *D3*. However, overall REE patterns are similar to those of *D1*. *D6-D7* REE patterns display a minor negative Ce anomaly, a minor negative Eu anomaly, MREE ‘bulge’ and HREE enrichment relative to the LREE’s but a depletion relative to the MREE’s (Figure 7.5). REE patterns from samples directly in a fault zone (7525.14b) display similar overall REE patterns but a more irregular trend between individual REE’s (Figure 7.5). *D6-D7* display average Sr isotope ratios of 0.708840 (Figure 7.6a).
Host rocks
Carboniferous limestone host rocks were selected for Sr isotopic analysis to determine whether they could have provided a source of Sr for dolomitisation. Sr isotope ratios range from 0.707906 to 0.707937 (Figure 7.6a). The results indicate that an insignificant amount of Sr was supplied to the dolomitising fluid, and therefore it is likely that an external source of Sr was responsible for the measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Sr concentrations.

East Irish Sea basin rocks
Samples of Namurian basin al mudstone were collected from core. In the absence of suitable Holywell Shale samples, samples were collected from the age equivalent Bowland Shale in the Preese Hall 1 core (see Appendix 1). The samples were selected to be representative of sediment deposited adjacent to the North Wales Platform during the Carboniferous, since the East Irish Sea Basin has been considered as the source of the mineralising fluids for the North Wales Platform (e.g. Dunham, 1970). A single Sr isotope ratio was obtained, 0.708009 (Figure 7.6a). This signature is less radiogenic than for the dolomitised limestone, but is more radiogenic than the platform carbonates.

7.6 Discussion
This study outlines a complex paragenetic sequence of dolomitisation for the North Wales platform margin succession of the Great Orme, UK. The paragenesis was constructed from the superposition and cross-cutting relationships of cements, diagenetic and structural features determined by field and petrographical analysis (Juerges et al., in prep, chapters 5 and 6). Subsequently, stable isotope and element geochemistry has been utilised to further characterise the cement phases and assess the potential sources of fluid and controls on precipitation (Juerges et al., in prep, chapter 5). From the petrographic and geochemical data presented,
at least three diagenetic environments have been identified: early shallow burial, early moderate burial and deep burial.

*Early shallow to moderate burial (D0 to D2)*

Mimetic and fabric retentive replacement of limestone by dolomite phases D0 to D2, took place preferentially within platform margin facies (packstones to grainstones) in the Pier Dolomite Formation (Juerges et al., in prep, chapter 5). Preferential replacement of crinoid grains by D0 was followed by pervasive replacement of coarse grained facies, rich in crinoid debris. The planar-s to planar-e textures, with unit extinction, exhibited by D0-D2 dolomite are typical of crystal growth at relatively low temperatures (<50°C) (e.g. Sibley & Gregg, 1987; Flügel, 2004). Dolomitisation pre-dates pressure solution and effective porosity would have been available assuming that early diagenetic calcite cementation had not completely occluded porosity. Elsewhere on the North Wales Platform, the Lower Carboniferous was subject to pervasive marine-meteoric calcite cementation that occluded the majority all interparticular porosity (Al-Fadel, 1983; Juerges et al., in prep, chapter 5). Should the limestone have been cemented prior to dolomitisation, then effective fluid flow pathways would have been destroyed. In addition, the coarse nature of the pore-occluding cements would have lowered the reactive surface area (e.g. Whitaker et al., 2010) and further inhibited dolomitisation. This suggests that dolomitising fluids exploited the relatively good, primary depositional, porosity and permeability of these facies, with seeding of dolomite focussing on high Mg$^{2+}$ allochems (e.g. crinoids and echinoids).

It is suggested, therefore, that the preferential replacement of coarse grained Asbian limestone was controlled by porosity, permeability, sediment composition, and presence of an effective fluid flow pathway (i.e. fault/fractures). Phases D0-D2 terminate against fractures, below mudstone beds but also within mud and wackestone beds without a reaction front. These terminations suggest the fine grained beds acted as effective permeability baffles in controlling fluid migration and facies variation within beds limited the lateral migration of fluid, combined with
dissipating temperatures, resulted in limited dolomite precipitation. Assuming that dolomitisation took place prior to the onset of pressure solution (at <300m; Sibley & Gregg, 1987), with the burial history curve this indicates that dolomitisation would have occurred during the Brigantian-Namurian. Although no direct relationship has been observed between D0-D2 and structural features these relatively early diagenetic dolomite phases occur in isolated pods along the northern platform margin that can only be explained by the presence of structures channelling fluid onto the platform. These phases are then dissected by several generations of faults and fractures that have been attributed to Variscan compression (Late Carboniferous-Early Permian) and subsequent tectonic movement (Juerges et al., in prep, chapter 5; Juerges et al., in prep, chapter 6).

When viewed using plane light, D0-D2 dolomite phases display progressive overprinting, gradual fabric destruction and an increase in crystal turbidity and rhombic habit. These are all suggestive of increasing temperatures and continued replacement of successive dolomite phases (e.g. Sibley & Gregg, 1987; Saller et al., 2011). In this sense, D2 represents precipitation at moderate burial depths with fabric destruction and evidence for fracture controlled distribution. Under CL, however, D0-D2 exhibits homogenous, dull luminescence suggesting a lack of geochemical variation between these early phases (Figure 7.3). This is further supported by the stable isotope, major ion and REE concentrations and Sr isotope data all show little variation. Since D0-D2 can be differentiated in plane light, with fabric retention and ghost allochems, it is unlikely that they have been recrystallised. More likely, dolomitisation took place from the same, or a geochemically similar, fluid. The REE profile is characteristic of seawater, which is confirmed by the presence of a negative Ce anomaly and the absence of an Eu anomaly which suggests oxidising conditions. Concentrations of Mn/Fe are low, also suggesting oxic porewaters. In addition, the Sr isotopic signature is very close to seawater curve for Namurian (Figure 7.6). The source of the
dolomitising fluids for phases D0-D2 has been interpreted as Brigantian-Namurian seawater.

**Deep burial (D3 to D5)**

Dolomite phases D3 to D5 comprise coarsely crystalline cements that occlude fault and fractures throughout the Asbian-Brigantian succession on Great Orme, but concentrated within the Pier Dolomite Formation (see Juerges *et al.*, in prep, chapter 5). Cross-cutting relationships with stylolites suggest crystal growth at burial depths of >300m (e.g. Sibley & Gregg, 1987). The coarse saddle textures indicate elevated temperatures >60°C (Radke & Mathis, 1980). The burial history curve indicates that the Dinantian/Namurian unconformity on the North Wales Platform reached a maximum burial depth of 1 to 1.5km in the Late Carboniferous, implying temperatures of between 55°C and 70°C assuming an ambient surface temperature of 25-30°C and a geothermal gradient of 30°C/km (Al-Fadel, 1985; Floodpage, 2001). However, it is possible that fluids were significantly hotter than 60°C, and were potentially hydrothermal, as a result of deeper burial in the basin and/or elevated heat flows along fault and fracture systems. In addition, high heat flow environments such as a syn/early post-rift environment can result in fluid circulation through faults at relatively shallow depths <1.5km (Robb *et al.*, 2005).

D3 to D5 cementation occurred primarily within bed parallel *en echelon* veins in the Pier Dolomite Formation and N-S and NE-SW orientated faults and fractures that have been attributed to the Variscan compression (Juerges *et al.*, in prep, chapter 6). The fault and fracture networks most likely acted as fluid flow conduits following occlusion of primary porosity by early calcite and dolomite cements (see Juerges *et al.*, in prep, chapter 6). Moreover, petrographic analysis reveals bridging textures within the fractures (mainly D3) suggesting that dolomite cementation took place during fracturing (e.g. Laubach, 2010).

The coarsely crystalline D3 saddle dolomite crystals are commonly in optical continuity with the host-rock dolomite (D0 to D2) of the Pier Dolomite Formation suggesting overprinting and/or precipitation from a
geochemically similar fluid or continued precipitation from the same fluid resulting in overdolomitisation. This is consistent with CL observations that display relatively homogenous red luminescence with rare, minor zonation. Minor etching, crystal edge effects and zonation are more apparent prior to precipitation of D4 and D5, which is attributed to disequilibria with the previous dolomite phase related to a change in parental fluid composition/source. This is also consistent with increasing turbidity and iron rich inclusions in the dolomites crystals with each successive phase suggesting increasing influence of burial fluids.

In combination, a shift to more Negative δ¹⁸O for D3-5, compared to D0-2, and slight an increase in Fe and Mn concentration and ratio (Table 7.5) points to an increase in fluid temperature and a change from an oxidising to reducing environment respectively, most likely as a result of burial. Based on an average δ¹⁸O_dolomite of -6.3 ‰ VPDB and a fluid temperature of 50 to 80°C, a δ¹⁸O_water of -2.9 and 2.0‰ SMOW can be calculated, which is typical of a more evolved fluid than for D0-2. δ¹³C values for D3-5 continue to cluster around typically marine values, suggesting dolomite cementation from marine porewaters with negligible rock buffering from minor dissolution of the previous dolomite phases (Figures 7.4, Table 7.3). When plotted on the graph in figure 7.4C the results indicate potentially higher temperatures than the estimated 50 to 80°C (e.g. 80-110 °C). In addition, non-luminescent cements with iron-rich coatings indicate precipitation from iron rich fluids potentially derived from the basin (Figure 7.3).

The rare earth element profile for D3-D5 dolomite has a broad seawater response, with a negative Ce anomaly, but the slight positive Eu anomaly and MREE bulge is suggestive of anoxic conditions. The Sr isotope ratios for D3-D5 show an increase in radiogenic Sr compared to phases D0 to D2, and are significantly enriched in radiogenic strontium when compared to Carboniferous seawater values (Figure 7.6). It is therefore suggested that D3-D5 dolomitisation took place from evolved marine porewaters. One mechanism for achieving this would be through clay diagenetic reactions in the juxtaposed East Irish Sea Basin, which has been
postulated as a source of fluid for mineralisation (e.g. Ixer & Vaughn, 1993). This is supported by burial history plots produced by Al-Fadel (1983) and Floodpage (2001) that suggests that during the Namurian, Dinantian siliciclastic sediments would have been at temperatures of >60°C.

**Burial and remobilisation (D6 to D7)**
Phases D6 to D7 were observed within the Great Orme Limestone, Bishops Quarry and Summit Formations as a passive fracture fill that occasionally replaces micritised allochems within the adjacent host-rock limestone (up to 0.5cm away from the fracture). D6-D7 superficially resembles phases D3-D5 although, a number of key differences are observed. D6-D7 weathers pink-brown in outcrop compared to toffee brown of the earlier phases. CL reveals bright luminescence as a result of elevated Mn, and low Fe, concentrations (Table 7.5). Cross-cutting relationships between D6 and D7 dolomite, with D3-5 dolomite, have not been observed in outcrop or polished section, thus a genetic relationship between them cannot be ruled out.

Stable Isotope values and geochemistry point towards a burial environment, although δ¹³C are slightly depleted (Figure 7.4, Table 7.3). Calculated δ¹⁸O water values range from -2.4 to 2.6 ‰ SMOW with estimated temperatures of 50-80°C suggest near Lower Carboniferous marine values. REE values display a modified seawater trend and are consistent with a reducing environment. However, Sr isotope values are not as radiogenic as the earlier dolomite phases suggesting potential waning of clay diagenetic reactions in the basin but more likely the influence from surface derived fluids as supported by the carbon isotopes.

**Overprinting and complexation**
Petrographic and trace element analysis demonstrates early calcite cementation, several episodes of dolomite precipitation and overprinting. It is suggested that the precursor limestone was low in REE’s while later
fluids were low temperature but received their REE and Mg within an elevated temperature/burial environment (e.g. Banner, 1988; Northdruft et al., 2004). During ascent the fluid cooled and reduced the capacity for complexation, resulting in lower REE concentrations. This is also supported by low trace element concentrations and especially a reduction in Sr concentrations with successive dolomite phases, which is indicative of overprinting. This interpretation suggests that the early phases (D0-D2) of replacive dolomite resulted from modified seawater and also inherited an REE signature from the precursor limestone. REE patterns and petrographic analysis in later dolomite phases (D3-D5) indicate that they precipitated from evolved formational fluids that encountered an environment with elevated temperatures and Sr was most likely gained through clay diagenetic reactions in the basin. This would have most likely occurred during burial and points towards a basinal fluid source. Further, an increase in Fe$^{2+}$ towards dolomite crystal boundaries and within succeeding dolomite phases requires a reducing environment (burial). MREE enrichment compared to LREE and HREE’S has been attributed to the presence of Fe-oxides efficiently scavenging REE’s (Klinkhammer et al., 1983; Johannesson et al., 1996; Sherrel, 1999) and releasing them within a reducing environment (Haley et al., 2004). The Fe-oxides can be present as grain coatings or inclusions within the crystals (e.g. Palmer & Edlerfield, 1986; Johannesson et al., 1996). This model is supported by enrichment in radiogenic Sr with each phase of dolomite, compared to the host-rock limestone. LREE depletion and HREE enrichment patterns indicate overprinting and potential remobilisation of dolomite (Bau & Moller, 1992). The results are supported by low Sr concentrations with increasing LREE depletion. Similar results have been observed in Lower Carboniferous dolomites from the Czech Republic (Kucera et al., 2009).

**Strontium source, transport and contamination**

The $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios measured within the dolomitised limestone and dolomite cements on the Great Orme evolve through the paragenetic
sequence, becoming more radiogenic with successive dolomite phases (Figure 7.6). Ratios range from 0.708841 to 0.709409 and demonstrate similar Sr sources.

During fluid-rock interaction Sr would have been released to the dolomitising fluid from limestone, and interbedded sand and mudstone units within the East Irish Sea Basin during clay diagenesis. $^{87}\text{Sr} / ^{86}\text{Sr}$ isotopic ratios for each of these lithologies are 0.7079215, 0.710095 and 0.708034, respectively. When compared to the dolomite values it is likely that these units supplied Sr to the dolomitising fluid. Widespread replacement and overprinting of host-rock and successive dolomite phases indicates extensive fluid-rock interaction and potentially high rates of fluid flow. The least radiogenic lithologies are the host-rock limestone (Sr ratios for Bishops Quarry Limestone 0.707906; Tollhouse Mudstone 0.708034) whereas the most radiogenic lithology is the Craig Rofft Sandstone Member (0.710095). These sediments were likely to have provided only a minor source of contamination during fluid flow for fluids migrating downward and/or fluids that migrated upward through fault and fractures, breaching these units.

The Sr is mostly likely sourced from basinal brines as suggested by the increasing radiogenic signature of the dolomite. However, there is also a possibility of fluid mixing and Sr being sourced from surface fluids (seawater via faults/fractures) with minor contamination from rare interbedded siliciclastic units (e.g. D6-D7). This is consistent with mechanisms for fluid flow on the North Wales Platform (Juerges et al., in prep, structural diagenesis, chapter 6) and supported by studies of similar deposits adjacent to the Great Orme (Haggerty & Bottrell, 1997).

**Model for genesis**

Several phases of dolomite have been identified and the cross-cutting relationships and isotopic/geochemical analysis constrained dolomitisation and dolomite cements to post-rift thermal subsidence and onset of compression in Pennine Basin (Juerges et al., in prep, chapter 6). It has been suggested by Warren et al. (1984) that dolomitisation
along the North Wales coast occurred during lowstand conditions in the Early Carboniferous. An evaporative diagenetic environment may have encouraged the drawdown of Mg rich fluids and provided the right conditions for dolomitisation (Patrick & Russell, 1989). However, textural evidence such as coarse crystals and fabric destruction, fault/fracture relationships and the volume of dolomite contradict this mechanism (Smith & Simo, 1997). In addition, the North Wales Platform shows no evidence of evaporites (gypsum/anhydrite) that would be expected in an evaporative environment or that has been predicted as a result of reflux and/or dolomitisation on a high relief carbonate platform (Jones & Xiao, 2005; Whitaker & Xiao, 2010).

The isotopic and elemental data reported in this study demonstrate a paragenetic sequence that indicates that dolomitisation took place from early burial into the deep burial realm across the Great Orme. The phases display ranges in $\delta^{18}O$ and REE’s which suggest an evolved seawater type signature. The timing of dolomitisation as determined by petrographic analysis and field observations (cross-cutting relationships and texture) further suggest hydrothermal fluids are an unlikely source for the early dolomite phases (D0-D2). A seawater source could potentially provide a large quantity of Mg required for dolomitisation (Land, 1985). This could have been supplied to the platform either through evaporative reflux of seawater or by free or forced geothermal convection (Bjorlykke et al., 1988; Whitaker & Xiao, 2010). Since there is no evidence for evaporation within the Asbian and Brigantian, and given that replacive dolomitisation is focused in the coarsest, cleanest facies, an evaporative drawdown and reflux model is not considered viable. Indicators of low temperature formation from seawater correspond with recorded examples of geothermal convection, which has often been invoked as a mechanism for early dolomite formation at low (20-30°C) temperatures (Saller, 1984; Hendry et al., 2002), although higher temperatures (50-70°C) may be required (Machel, 2004). Reactive transport models suggest that geothermal convective cells can become established in relatively small platforms, 300-500m in height, such as that observed within North Wales
(Whittaker, pers. Comms. 2010). Moreover, dolomitisation would preferentially occur at the platform margin (Whitaker & Xiao, 2010). Dolomitisation is dictated by reactive surface area, heat flux and fluid flux, thus the preferential replacement of coarse grained shoaling facies may have been expected to inhibit dolomitisation through low reactive surface areas and loss of heat (e.g. Whitaker & Xiao, 2010). However, on the North Wales Platform dolomite precipitation was seeded on high Mg calcite grains, providing nucleation points in a high permeability facies, with flow focused beneath flow baffles/barriers. Sharp terminations are inconsistent with Mg depletion during dolomitisation (Saller & Henderson, 1998), and are less likely to be permeability controlled (as terminations are within beds). Therefore it is suggested that cooling and reduction in fluid flux away from fluid conduits controlled the termination of dolomite bodies (e.g. hydrothermal fluids, Davies & Smith, 2006). The mode of convection was most likely forced convection (Kohout convection) as free convection would have been inhibited by interbedded mudstones throughout the Pier Dolomite Formation. This is supported by a high concentration of dolomite at the base of the formation and the outcrop, the termination of replacive (D0 to D2) below the Toll House Mudstone Formation and overdolomitisation below mudstone bed baffles, consistent with an upward fluid flux. Dolomitisation by geothermal convection is a relatively slow process (Whitaker & Xiao, 2010) and within shallow burial environments and within coarse grained facies lower temperatures can reduce dolomitisation rates. This can be overcome by high fluid fluxes that can be established for long periods of time (24-42 kg/day/m) (Sanford et al., 1998).

Phases D3 to D7 precipitated from formation fluids expelled from the basin. The relationship to stylolitisation illustrates a post-maximum burial timing and occurrence within faulting and fracturing that indicate precipitation during burial and the onset of compression (Juerges et al., in prep, chapter 6). These observations are consistent with the burial history proposed by Al-Fadel (1983). Moreover, a basinal source is consistent
with previous studies of the Great Orme (Ixer & Stanley, 1996) and with models for Lower Carboniferous fluid expulsion and dolomitisation that invoke a fluid source from juxtaposed hanging wall basins (Coleman et al., 1990; Ixer & Vaughan, 1993; Hollis & Walkden, 2012). Basin to platform migration is supported by the concentration of dolomite at the northern platform margin, diminishing southwards and occurrence primarily within faults and fractures that extend into the East Irish Sea Basin (Williams & Eaton, 1993; Juerges et al., in prep, chapter 6) (Figure 7.1). This is a trend that has also been observed elsewhere on the North Wales Platform where mineralisation (galena, sphalerite, fluorite and baryte) is intergrown with fault/fracture hosted calcite diminishes away from the platform margin (Juerges et al., in prep, chapter 5).

Field and petrographic observations demonstrate that much of the primary porosity was occluded during early diagenesis by dolomite phases D0 to D2 and calcite cements (Juerges et al., in prep, chapters 5 and 6). Therefore, fluid flow had to take place along fault and fracture systems. The presence of faults/fractures and a lack of matrix porosity and permeability rule out a convective fluid flow mechanism for phases D3-D5 meaning that fluids would have mostly migrated vertically through the succession. This is consistent with limited dolomitisation within host-rock limestone in the Great Orme Limestone Formation and overlying formations away from faults and fractures. Within the Pier Dolomite Formation D3 cements are associated with tensile fractures, zebra textures and brecciation that indicate high fluid pressures, flexure slip along beds and multiple reactivations of faults and fractures (Juerges et al., in prep, chapter 6). The build up of high pressures and multiple rupturing events reflects the lack of matrix porosity and destruction of fabric following precipitation of D0 to D2 and increasing confining pressures. Within the faults, brecciation and multiple cement fills and reactivations suggest potential fault valve action (e.g. seismic pumping, Sibson, 1995). Moreover, bridging textures within N-S fracture systems suggest precipitation during fracturing. These observations support compression related dewatering followed by a tectonic drive for fluid
expulsion (op. Cit.). The patterns of structural deformation follow Caledonian trends and align with stress directions imposed by the Variscan Orogeny (See Juerges et al., in prep, Chapter 6).

The petrographic, isotopic, geochemical results also rule out a later timing for dolomitisation (e.g. Triassic-Jurassic). Dolomite pre-dates Pennine style/MVT mineralisation on the North Wales, Askrigg and Derbyshire Platforms suggesting that dolomitisation occurred prior to or during the onset of Variscan tectonism (Lewis, 1996; Hollis, 1996; Hollis & Walkden, 2012). Peak mineralisation and fluid flow are suggested to have occurred during the Late Carboniferous (Ixer and Vaughan, 1993; Hollis and Walkden, 2002; Hollis & Walkden, 2012). During this period fluid compositions changed and primarily calcitic cements precipitated (Juerges et al., in prep, chapters 5 and 6). This could have occurred for a number of reasons including depletion of Mg and saturation of Ca during dolomitisation, a change in fluid source and/or a change of the physiochemical conditions. The discrete pods of dolomitisation along the North Wales Platform margin around select structural lineaments potentially tapped into an Asbian-Brigantian basinal fluid source early in the burial history that gradually became depleted. A switch to calcitic fluid during the onset of the Variscan Orogeny was potentially sourced from juxtaposition Late Brigantian- Namurian basinal fluids from which metal required for MVT mineralisation were also sourced (Juerges et al., in prep, chapter 6). Negligible volumes of cross-cutting MVT mineralisation around the Great Orme compared to NE Wales Orefield only occur next to local mudstone baffles suggesting that where the baffles do not occur metalliferous fluids could have escaped to the surface resulting in much lower volumes of MVT mineralisation. Following the Variscan the compressional fluid drive would have waned, limiting further fluid flow and resulting in a fluid depleted basin. In combination, these factors make later dolomitisation unlikely. (See Figure 7.7).
7.7 Conclusion

The data presented demonstrates a contribution to progressive porosity destruction by dolomitisation on the Great Orme, North Wales during the Early Carboniferous. Several generations of dolomite (D0 to D7) have been identified petrographically and further characterised geochemically and isotopically.

Early diagenesis was strongly facies controlled. Variations in porosity and permeability determined preferential fluid migration pathways. As a result cementation occluded much of the primary porosity soon after deposition or dolomitisation replaced the host-rock limestone. Syntaxial calcite cements and/or replacement dolomites are concentrated particularly within packstone and grainstone shoals. As a result, the distributions of subsequent diagenetic cements were controlled by the composition of the early diagenetic phases and the production and distribution of secondary porosity (i.e. fractures).

Geothermal convection of seawater and migration of formational fluids in late syn-rift and early post-rift resulted in the precipitation of matrix replacive D0-D2 at depths of less than 300m.

Expulsion of potentially overpressured basinal brines by fault rupture during post rift sag-subsidence and onset of inversion resulted in the precipitation of phases D3-D7), between depths of 300m to 1.5km. Fluids were potentially sourced from Lower Carboniferous basinal sediments.

The main phase of compression during the Late Carboniferous marked a change from dolomite cementation to calcite cementation and MVT mineralisation most likely due to a change in fluid source (from Lower Carboniferous to Namurian basinal sediments).

A second burial event occurred from the Triassic to Jurassic followed by uplift in the Early Tertiary. Pre-existing faults and fractures were
reactivated, partially remobilising phases D6 to D7 followed by the emplacement of copper mineralisation and calcite cementation.

Dolomitisation can have complex emplacement histories and often display overprinting of successive phases. This can make determining the source, timing and fluid flow pathways of the dolomitising fluids problematic using standard techniques. Thus it is recommended that a multiscale, combined techniques approach is adopted. Where stable isotope and element analysis is unable to fully characterise individual cement phases, Sr isotope and REE data is invaluable.

**Acknowledgement**

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Fig. 7.1. A) Regional map showing the study area, Great Orme Wales Platform, dolomite occurrences along the north Wales coast and position of the East Irish Sea Basin Modified from Jackson et al. (1993), B) Location map displaying the sampling positions and the locations of sedimentary logs, Great Orme, UK (adapted from Warren et al., 1984).
Fig. 7.2. Schematic palaeogeography across North Wales and stratigraphic log for the Great Orme (modified from Waters and Davies, 2006). Red dot: Great Orme.
Figure 7.3. Photopanel of the dolomite paragenesis for the Great Orme (A) Phases D0-D3, Pier Dolomite Formation, transmitted light, x4 (B) D1 and D3 cross-cutting relationship, Pier Dolomite Formation, transmitted light, x4 (C) D0-D1 and D3, showing fabric retentive crystals and saddle crystals respectively, Pier Dolomite Formation, transmitted light, x4 (MD: mimetic dolomite replacement of a crinoid fragment) (D) D3 displaying progressive replacement after D0-D2, Pier Dolomite Formation, transmitted light, x10 (E) CL image showing Phases D1-D5, little zonation between phases and decreasing luminescence with each successive phase, Pier Dolomite Formation, CL, x10 (F) CL image of showing D6-D7
cross-cutting a partially cemented fracture containing calcite (yellow-orange) and also partially replacing the adjacent host-rock limestone with rhombic terminations, Great Orme Limestone Formation, CL, x4.
Figure 7.4. Stable isotope data for the dolomite on the Great Orme A) Stable isotope data grouped by defined paragenetic phases; B) Stable isotope data grouped by location. All results are reported to the VPDB standard.

Figure 7.4C Plot of precipitation temperature versus $\delta^{18}O$ values of D0-D2, D3-D5 and D6-D7. The $\delta^{18}O$ composition of the fluid in equilibrium with dolomite as function of the temperature was calculated using the fractionation equation of Land (1983).
Figure 7.5. Shale normalised (PAAS) REE patterns for dolomite, unaltered whole-rock limestone and calcite (PAAS according to Nance and Taylor, 1976), Blue: LREE’s, Green: MREE’s, Red: HREE’s
### a)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Sample</th>
<th>87Sr/86Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>brachiopod</td>
<td>SMBC</td>
<td>0.707845</td>
</tr>
<tr>
<td>WR Lmst</td>
<td>7525.1</td>
<td>0.707937</td>
</tr>
<tr>
<td>WR Lmst</td>
<td>SM1</td>
<td>0.707906</td>
</tr>
<tr>
<td>WR clastic</td>
<td>THM</td>
<td>0.707934</td>
</tr>
<tr>
<td>WR clastic</td>
<td>SH</td>
<td>0.708009</td>
</tr>
<tr>
<td>D1-D2</td>
<td>AJ8</td>
<td>0.709042</td>
</tr>
<tr>
<td>D1-D2</td>
<td>PD5a</td>
<td>0.709251</td>
</tr>
<tr>
<td>D1-D2</td>
<td>767.2</td>
<td>0.708515</td>
</tr>
<tr>
<td>D1-D2</td>
<td>767.9</td>
<td>0.709245</td>
</tr>
<tr>
<td>D3</td>
<td>RSQ</td>
<td>0.70899</td>
</tr>
<tr>
<td>D3</td>
<td>THM</td>
<td>0.70903</td>
</tr>
<tr>
<td>D3-D5</td>
<td>PD5B</td>
<td>0.709409</td>
</tr>
<tr>
<td>D6-D7</td>
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<td>0.708442</td>
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<td>D6-D7</td>
<td>7525.2</td>
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<tr>
<td>D6-D7</td>
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<tr>
<td>clastic</td>
<td>CRL5.3</td>
<td>0.710095</td>
</tr>
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</table>

### b)

![Graph showing Sr/86Sr vs. Paragenesis](http://example.com/graph.png)
Figure 7.6. Summary of Sr isotope data (a) Table of Sr isotope values for the sample analysed (b) Sr isotope data plotted by paragenetic phases (c) Sr isotope plot – with comparative Dinantian seawater trends (grey boxes represent the dolomite phases from this study), CL: clastic lithologies, HR: host rock
Figure 7.7. Schematic diagram depicting the timing and interpreted mechanism of emplacement of dolomite and metalliferous mineralisation during early, syn and late rifting and then subsequent reburial during the Permo-Triassic, A) structural diagenetic phase 1, B) structural diagenetic phase 2, C) structural diagenetic phase 3, D) structural diagenetic phase 4, E) structural diagenetic phase 5, F) structural diagenetic phase 6. EISB: East Irish Sea Basin, Pb: galena, Zn: sphalerite, Cu: chalcopyrite, Dol: dolomite, (not to scale).
## Tables

<table>
<thead>
<tr>
<th>Cement</th>
<th>Morphology</th>
<th>CL</th>
<th>Extinction</th>
<th>Inclusion density</th>
<th>Inclusion type</th>
<th>Mineralisation</th>
<th>Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>D0</td>
<td>Mimetic</td>
<td>Medium pink/red</td>
<td>Unit</td>
<td>Turbid</td>
<td>Rare fluid</td>
<td>-</td>
<td>Echinoid</td>
</tr>
<tr>
<td>D1</td>
<td>Planar-s</td>
<td>Medium pink/red</td>
<td>Unit</td>
<td>Turbid</td>
<td>Fluid</td>
<td>-</td>
<td>Bioclastic wacke-packstones</td>
</tr>
<tr>
<td>D2</td>
<td>Planar-e</td>
<td>Medium pink/red</td>
<td>Unit, undulose</td>
<td>Turbid</td>
<td>Fe oxides</td>
<td>Fe oxides</td>
<td>D1 overprint, adjacent to extensional veins</td>
</tr>
<tr>
<td>D3</td>
<td>Planar-e, baroque</td>
<td>Medium pink/red</td>
<td>Undulose</td>
<td>Limpid</td>
<td>Fe oxides fluid</td>
<td>-</td>
<td>Extensional veins</td>
</tr>
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<td>D4</td>
<td>Baroque</td>
<td>Red</td>
<td>Undulose</td>
<td>Limpid-turbid</td>
<td>Fe oxides fluid</td>
<td>-</td>
<td>Extensional veins</td>
</tr>
<tr>
<td>D5</td>
<td>Xenotopic</td>
<td>Red</td>
<td>Unit &amp; undulose</td>
<td>Limpid-turbid</td>
<td>-</td>
<td>Chalcopyrite</td>
<td>Extensional veins and passive fill</td>
</tr>
<tr>
<td>D6</td>
<td>Planar-s, baroque</td>
<td>Dark red-brown</td>
<td>Undulose</td>
<td>Turbid</td>
<td>Fe oxides Fluid, solid</td>
<td>Fe oxides</td>
<td>Mixed mode veins around normal and strike-slip faults</td>
</tr>
<tr>
<td>D7</td>
<td>Xenotopic, diffuse</td>
<td>Bright pink</td>
<td>Undulose</td>
<td>Turbid</td>
<td>Fe oxides Fluid, solid</td>
<td>Fe oxides</td>
<td>Mixed mode veins around normal and strike-slip faults</td>
</tr>
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</table>

Table 7.1. Summary dolomite paragenesis and petrographic characteristics
Chapter 7

Table 7.2. Summary of faults/ fractures, cement association and orientation

<table>
<thead>
<tr>
<th>Set</th>
<th>Orientation</th>
<th>Cement</th>
<th>Phase</th>
<th>Mineralisation</th>
<th>Kinematic mode</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>N-S</td>
<td>Dolomite, calcite</td>
<td>C5-C13, D3</td>
<td>Cu-Fe-Pb-Zn</td>
<td>opening + mixed</td>
</tr>
<tr>
<td></td>
<td>NNW-SSE</td>
<td>Dolomite</td>
<td>D3</td>
<td>-</td>
<td>opening + mixed</td>
</tr>
<tr>
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<td>NNE-SSW</td>
<td>Dolomite</td>
<td>D3</td>
<td>-</td>
<td>opening + mixed</td>
</tr>
<tr>
<td>2</td>
<td>E-W</td>
<td>Calcite, dolomite</td>
<td>C12+, D6, D7</td>
<td>-</td>
<td>opening</td>
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<tr>
<td>3</td>
<td>NW-SE</td>
<td>Calcite and dolomite</td>
<td>C5-C13, D3, D6, D7</td>
<td>Pb-Zn</td>
<td>opening + mixed</td>
</tr>
<tr>
<td>4</td>
<td>NE-SW</td>
<td>Calcite</td>
<td>C5-C13</td>
<td>-</td>
<td>opening</td>
</tr>
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</table>

Table 7.3. Stable isotope analysis WR: Whole Rock,

Analytical error ± 0.1‰ (2σ)
### Table 7.4. Calculated SMOW values, using the Equation of Land (1983).

<table>
<thead>
<tr>
<th>Phase</th>
<th>°C</th>
<th>10^3 ln(dol-water)</th>
<th>VPDB</th>
<th>Dolomite SMOW</th>
<th>Water SMOW</th>
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<tr>
<td>D0-D2</td>
<td>30</td>
<td>303.15</td>
<td>-6.64</td>
<td>24.07</td>
<td>-7.45</td>
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<td></td>
<td>40</td>
<td>313.15</td>
<td>-6.64</td>
<td>24.07</td>
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<td></td>
<td>50</td>
<td>323.15</td>
<td>-6.31</td>
<td>24.40</td>
<td>-2.94</td>
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<td></td>
<td>60</td>
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<td></td>
<td>70</td>
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<td>-6.31</td>
<td>24.40</td>
<td>2.04</td>
</tr>
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<td>-5.80</td>
<td>24.93</td>
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</tr>
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<td>333.15</td>
<td>-5.80</td>
<td>24.93</td>
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<td>343.15</td>
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<td>24.93</td>
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<td>353.15</td>
<td>-5.80</td>
<td>24.93</td>
<td>2.57</td>
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### Table 7.5. Overview of trace element concentrations in dolomite, calcite and whole rock (WR) samples for the Great Orme

<table>
<thead>
<tr>
<th>Trace elements</th>
<th>Mg (ppm)</th>
<th>Fe (ppm)</th>
<th>Sr (ppm)</th>
<th>Mn (ppm)</th>
<th>Measuring device</th>
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<tbody>
<tr>
<td>D1</td>
<td>267.65</td>
<td>14.61</td>
<td>0.06</td>
<td>5519.13</td>
<td>ICP-AES</td>
</tr>
<tr>
<td></td>
<td>268.27</td>
<td>11.35</td>
<td>63.59</td>
<td>5532.93</td>
<td>ICP-MS</td>
</tr>
<tr>
<td>Average</td>
<td>267.96</td>
<td>12.98</td>
<td>31.83</td>
<td>5526.03</td>
<td>Microprobe</td>
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<tr>
<td>D1-D2</td>
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<td>12.49</td>
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<td></td>
<td>344.01</td>
<td>21.46</td>
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<tr>
<td>Average</td>
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<td></td>
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Chapter 8: Synthesis
Chapter 8

8.0 Synthesis and Conclusions

This thesis aimed to provide a diagenetic framework for the North Wales platform and evaluate the porosity evolution, in particular during burial diagenesis. Focus was on cements within small fractures (between 0.1 and 2 cm) and occlusion of interparticular porosity following extensive meteoric diagenesis.

The problems and objectives were outlined at the beginning of the thesis. This chapter endeavours to summarise and synthesise the conclusions and relevant results from previous chapters. Finally, the findings will be discussed with regards to the wider implications and recommendations for future work will be presented.

8.1 Depositional setting

8.1.1 Carbonate platform

Platform top and platform margin carbonate environments have long been recognised as excellent records of syn-depositional sea-level variation as carbonate-secreting flora and fauna are very sensitive to changes in environment such as light and temperature and require subaqueous conditions. Facies and pre-burial diagenesis exert a strong control on subsequent patterns of burial diagenesis.

The Lower Carboniferous North Wales Carbonate Platform records an evolution from a ramp to rimmed platform by the Asbian (Somerville et al., 1989). Within this study a range of inner platform, cyclic facies have been observed around Llangollen which support the previous studies of Smith (1927), Gray (1981) and Somerville et al., (1989). The overlying Minera Formation display ooidal grainstone shoals that form tidal channels established under a higher energy regime. Transgressive –regressive cycles are recorded within the Asbian and Brigantian succession that are most likely a result of glacio-eustacy. This conclusion is derived from the
regular and short scale patterns that have been observed elsewhere in the UK.

8.1.2 Basinal succession

The predominantly siliciclastic Permo-Triassic and Jurassic successions of the East Irish Sea Basin are well described as a result of hydrocarbon industry interest following a number of oil and gas field discoveries (e.g. Meadows et al. (1997) and references therein). However, the underlying Carboniferous stratigraphy has not been investigated and sampled to the same extent. The Carboniferous basinal succession comprises the Garwood and the Bisat Groups (Dinantian and Namurian respectively) (Ramsbottom et al., 1978). These units have been defined mainly from well log analysis, scarce biostratigraphy and analysis of the onshore North Wales Platform equivalents (Jackson et al., 1997). However, no formal lithostratigraphic or chronostratigraphic correlation has been achieved to date (op. Cit.). The lack of data for the Carboniferous succession in the East Irish Sea Basin is in contrast to that available for the adjacent Bowland Basin, Lancashire and Edale, Widmerpool and Craven basins in Derbyshire (Hollis, 1996). In order to evaluate the basinal succession within combined published data and data collected during the course of this study from the adjacent Bowland basin were applied (see chapter 4).

8.2 Summary of diagenetic observations, North Wales Platform

The diagenetic overprint observed on the North Wales Platform is complex and controlled by the composition of the host-rock limestone and development of secondary porosity in the form of fault and fracture networks.

*Marine* diagenesis occurred during and soon after deposition and is very rare. Marine cements that have been observed occur within ooidal and shoaling facies and reef and crinoid build-ups at the platform margin (Great Orme and the Little Orme) (see also Bancroft, 1986). This may be a result of sampling bias, an initial lack of marine cementation or
destruction and overprinting by the dominant meteoric phases. It is most likely that the scarcity in observation is a combination of the first and second points. This study was conducted with a view to assess the burial diagenesis and therefore more emphasis was placed on sampling in and around fracture systems. The fault and fracture systems were created after lithification of the Lower Carboniferous succession and have been observed to host burial cements.

The low energy lagoonal and platform top depositional environments that dominate most of the study localities would not have favoured the occurrence of isopachous marine cements and without detailed isotopic analysis the origin of the blocky and isopachous calcite cements observed remains ambiguous. Petrographic analysis displays concentrically zoned bright and non-luminescent cements suggesting a meteoric origin (see chapter 5).

*Meteoric* burial is widespread throughout the North Wales Platform and occludes most of the primary interparticle porosity with bladed, blocky and syntaxial calcite cements. They occur primarily within the lagoonal and platform top successions.

*Burial* from shallow to deep burial a number of variations in the style of diagenetic overprint has been observed. This has been controlled by the composition of the sediments, the poor preservation of porosity throughout much of the platform, proximity to secondary porosity and fluid flow conduits and proximity to diagenetic fluids sources such as basinal brines.

*Telogenesis* is only observed at the platform margin where modification of the porosity and permeability related to dolomitisation has enabled later diagenetic and surface derived fluids to infiltrate the host rock carbonate especially in close proximity to faults and fractures.

*Comparison with the Derbyshire and Askrigg Platforms*
The early marine and meteoric diagenesis is similar between the different platforms. Variation in cement type and distribution becomes more evident during burial where different basinal fluid sources are utilised.

8.3 Fluid flow and cementation

8.3.1 Element source, transport and release

8.3.1.1 Dolomitisation

The dolomitisation of the Lower Carboniferous succession on the North Wales Carbonate Platform is concentrated along the platform margin, which is located along the current day coastline. The different dolomite phases identified the most likely source for Mg is from seawater either circulating through more porous facies soon after deposition and the through faults and fractures during burial. This is supported by petrographic textures and stable isotope data that indicate elevated temperatures with successive dolomite phases. These observations are also further supported by cross-cutting relationships with burial compaction features such as stylolites. Magnesium is also potentially derived from the breakdown of detrital minerals in the basin although the amount of magnesium is unlikely to be able to account for the extent of mineralisation. Localisation of the dolomitisation can be explained by the compartmentalised fluid and therefore element sources within the EISB. This could also explain the different phases of dolomite but a similar source, as suggested by the geochemical analysis. However, further study would be required to confirm this.

8.3.2 MVT mineralisation

Elements responsible for cementation and mineralisation were derived from the platform limestone, local mudstones and Namurian basin shales. The shales would have provided Zn, Pb, Cu and minor F, whereas, Ba is most likely derived from clays within the basin and overlying siliclastic successions. Permo-Triassic sandstones would have sourced Cu for the
second mineralisation event with minor Zn, Pb. These elements could have been released during burial, the breakdown of detrital material and the clay diagenesis.

### 8.3.3 Copper

Cu was sourced from overlying Permo-Triassic sandstones with potential minor input from the platform and basin limestone released during fluid-rock interaction and dissolution-precipitation events. Mg for the dolomitisation was derived from modified seawater retained within the pore-spaces and from basinal fluids during burial. Cl, stable isotope and REE observations indicate overprinting and remobilisation of dolomite during sequential replacement (D0 to D7).

### 8.3.4 Sulphur

The source of sulphur for the mineralisation is not well constrained and based on circumstantial evidence. Due to the lack of evaporites within the North Wales platform succession, sulphur would have been sourced from formational fluids, minor volumes from maturation of organic matter during burial. It is possible that evaporites existed and were removed or altered during burial diagenesis, however, there is no textural or evidence leaching that may suggest this is the case. Sulphur isotope analysis is lacking from the mineralisation from the NE Wales Orefield, although, temperatures of 105 to 130°C (fluorite fluid inclusion data, (Smith, 1973)) would also rule out bacteria reducing processes (Robinson & Ineson, 1979). Limited hydrocarbon evident across the North Wale Platform suggests that any input of light $^{34}$S would be localised and minor.

Fluid inclusion data from fluorite in the Halkyn District indicates that the fluids responsible for mineralisation were connate sodium chloride brines (Smith, 1973). Additional, data from Parnell (1983, 1988a) and Parnell & Swainbank (1990) document the inclusion of solid hydrocarbon within fluorite and associated with Pb-Zn mineralisation. Moreover, the mineralising fluids and hydrocarbon most likely migrated at the same time
(Parnell & Swainbank, 1990). If this is the case then the elements were likely to have been transported in complexes with the chloride and/or hydrocarbon.

8.3.5 Summary of fluid migration pathways

The lack of fluid inclusion data for the calcite cementation means that the composition of the fluids responsible cannot be fully constrained. However, the primary source of fluids for cementation and mineralisation would have been formational fluids that were initially circulating through the primary porosity in the succession. During burial compaction would have contributed to the dewatering of the basin and supported by the lack of evidence for overpressuring during meteoric diagenesis. Following extensive cementation, compressional tectonism during the Variscan Orogeny could have then squeezed basin fluids on to the North Wales Platform via fault and fracture systems. Following uplift and fluid expulsion, aquifer and surface derived fluids may have migrated downward into the platform limestone within reactivated faults via gravitational mechanisms.

Early diagenetic products, which occlude primary porosity, reduced the number of fluid flow pathways. Moreover, the mechanical properties of the rocks were modified and Late Carboniferous-Early Permian compression resulted in deformation. The newly formed and reactivated faults would have provided effective conduits for fluid flow. Fluid was expelled mainly from the East Irish Sea Basin along N-S and NE-SW faults. Fluids were also potentially expelled from a secondary source, the Cheshire Basin, on to the NE platform margin. Fluids from the Cheshire Basin would have exploited NE-SW and rare E-W faults and lineaments (e.g. Bala Lineament). The overall fluid migration trends observed on the North Wales Platform is oriented N-S.

8.3.5.1 Dolomitisation: convective vs. compaction and Reflux fluid flow
Convection, compaction and reflux are mechanisms for the flow of seawater or formational fluids under varying hydraulic head. They are mostly active during early stages of diagenesis although convective and compactional fluid migration can also be active during burial.

Evidence for reflux flow within Carboniferous Platform settings is mostly absent (e.g. Van der Kooij et al., 2007). This is supported by the field and petrographic observations for the North Wales and Derbyshire/Askrigg Platforms. Although early phases of dolomite have been identified there is a general lack of by products such as evaporites that may be expected with this flow mechanism (Jones et al., 2000). In addition, isotope results indicate elevated temperatures of these early phases during precipitation and are geochemically similar to later burial phases. Surface derived fluids during reflux would not have been elevated in temperature. Similarly, with a compactional mechanism it is likely that any elevated temperatures of the fluids would have dissipated during fluid migration (Whitaker & Xiao, 2004). A convective migration mechanism could have become established at the platform margin as a result of thermal gradients. This would have enabled the circulation of modified seawater held within the Lower Carboniferous succession and the upward migration of basinal derived fluids (sources for Mg), via fault and fracture networks, for an extended period of time. The fluid flux, availability of Mg and elevated temperatures would have favoured dolomitisation. Forward modelling would be a way of testing these different scenarios. However, this was beyond the scope of this study.

8.3.6 Summary mechanisms for cementation/precipitation

- A range of mechanisms are likely to have resulted in mineralisation and cementation, these include:
  - Temperature and pressure reduced during faulting and fracturing
  - Saturation in fluids respect to CaCO$_3$ or CaMg(CO$_3$)$_2$
- Mixing of fluids and/or breakdown of complexes

8.4 Overpressuring

Overpressuring on the North Wales Platform has not been previously investigated or reported. Furthermore, the lack of sedimentological data for the Carboniferous basinal succession within the EISB, makes it difficult to assess the potential and extent of overpressuring. Field evidence from the Great Orme suggests that fluids may have been overpressured. Evidence includes zebra textures and fault hydro-breccias (see chapter 6). Overpressuring could have potentially developed within the basinal limestones and impermeable mudstone in the EISB (Holywell Shale) adjacent to the North Wales Platform as a result of rapid sedimentation during extension. This would have retained fluids within the basin until the onset of faulting and fracturing during the Variscan compression and basin inversion (see the following section). Similar mechanisms were postulated by Hollis & Walkden (2002) supported by recent advances in the regional basin models.

To the east of the study area (Prestatyn) the fine grained basinal limestone and shale successions are also evident (Williams & Eaton, 1993) however, there is a notable increase in siliclastic material especially around the Point of Ayre (Jackson et al., 1997). This variation in basin sediment composition could have lead to early migration of fluid out of the shales and in part explain why features such as zebra veining and fault breccia, attributed to overpressuring, are not as evident in comparison to the Great Orme.

Compartmentalisation related to faulting and fracturing and pervasive early cementation on the North Wales Platform was also possible. This is in part supported by the variation in MVT and gangue cements volumes across the North Wales Platform. It is also well documented that many of the fault systems were active during sedimentation in the Lower Carboniferous and subsequently reactivated multiple times.
A way of testing this would be to compare the salinities of the calcite cement phases across the North Wale Platform. Overpressured fluids would be of greater temperature and higher salinity compared to normally pressurised fluids and should thus display contrasting fluid inclusion data (Bradley, 1975). There is no available fluid inclusion data to test this and within the scope of this study no suitable fluid inclusions were identified during petrographic analysis.

8.5 Conceptual structural and diagenetic model

Within chapters 5 to 7 it has been proposed that early calcite cements that predominantly occlude primary porosity were due to marine and meteoric fluids. These resulted from the establishment of aquifers throughout the Dinantian, primarily controlled by sea-level fluctuations. This early diagenesis occurred during a phase of regional extensional tectonism and is evidenced by the occurrence of fibrous fringing cements and syntaxial overgrowths within upward shoaling platform facies to peritidal facies, with frequent exposure surfaces that characterise the platform. Subsequent fluid flow took place within the burial environment from modified seawater and formational fluids that exploited secondary fluid flow conduits such as faults and fractures. The early diagenetic events modified the host-rock limestone that comprised the North Wales Platform. This resulted in a reduction in effective flow pathways and an increase in the brittle nature of the units. Therefore, towards the end of the Carboniferous as extension began to wane and the onset of N-S Variscan compression took hold, pre-existing lineaments were reactivated and new networks developed. These structures display normal and strike-slip movement with associated brecciation. Fault/fracture dilation and brecciation could have provided suitable porosity and permeability within the fault zones for fluid to migrate through. However, there is limited matrix porosity/permeability away from fault damage zones where fracturing and mineralisation within the host-rock limestone is rare.
Geothermal convection has often been invoked as a mechanism for fluid flow during early burial diagenesis. However, the process requires a body of rock relatively free of discontinuities and permeability barriers. In contrast, fault related fluid circulation can access basin fluid sources and well as providing conduits for the downward migration of surface derived fluids and/or upward migration of basinal or formational fluids. The vertical extent down to depths from 100’s of metres to kilometres, association with crustal thinning during extension and establishment of gradients can provide heat required to drive fluids through these conduits. The fault related mechanism is consistent with structural and diagenetic observations across the North Wales Platform. Burial cements (calcite and dolomite) that have negative $^{18}\text{O}$ values, modified seawater REE patterns and radiogenic Sr isotopic signatures, suggestive of a basinal source, precipitated within select fault/fracture systems. Moreover, the cements are concentrated within the lower portions of the Asbian-Brigantian succession within coarser grained shoaling facies and display ponding below permeability barriers. These observations point towards fluid flow from the basin on to the platform via lineaments that were active during the Late Carboniferous. As fluids ascended the change on pressure and temperature could have caused cementation. Pods of dolomite replacing Asbian limestone occurred around some active faults and with fluids derived from potentially compartmentalised basin successions (Dinantian carbonates and Namurian Holywell Shales). As cementation and dolomitisation developed fluids were potentially expelled by overpressuring and seismic pumping along fault systems, accessing different slightly different fluids and compositions. Similar mechanisms have been invoked for the Derbyshire Platform and supported by preliminary burial and fluid flow models (Frazer et al., 2012.). This is supported by increasing radiogenic Sr signatures and REE patterns that suggest basinal brines. Elsewhere on the platform either the faults were not active, didn’t have access to Mg charged fluids or kinetic conditions inhibited widespread dolomitisation and calcite cements were precipitated instead. Where the dolomitisation occurred, fluid migration started prior to
the onset of Variscan compression preferentially replacing upward shoaling units containing abundant crinoid and coral debris thus a high Mg\(^{2+}\) precursor and heterogeneity/sediment roughness are considered to be controlling factors on where dolomite seeded. A basinal source with elevated temperatures for the burial diagenetic products is in agreement with the temperatures suggested by the burial history (Al-Fadel, 1985; Hardman et al., 1993) and can account for the negative \(^{18}\)O values measured in the cements and the suggested values for the precipitating fluids. In addition, there is a general decrease in dolomitisation, burial calcite cementation and mineralisation away from the platform margin.

Cross-cutting veins containing Pb-Zn mineralisation was precipitated in faults and fractures following Variscan trends. Previous studies have suggested a basinal source for the mineralising fluids and high salinities (Smith, 1973). Furthermore, analysis of hydrocarbon inclusions within the mineralisation has suggested that they were coeval and that the source was the Holywell Shale within the East Irish Sea Basin. Retention of fluids within the basin was most likely a result of deposition of impermeable units limiting any dewatering that may have occurred early in the diagenetic history. Finally, lead dating techniques have produced dates of between 240 and 248 Ma (Permo-Triassic) for the mineralisation in the NE Wales Orefield and a mid-Carboniferous age has been deduced for mineralisation within the Llanrwst and Llanfair Orefields (Haggerty & Bottrell, 1997). Although the Permo-Triassic dates have been called into question, the data provides an upper constraint on the mineralisation and dolomitisation on the North Wales Platform. Carboniferous mineralisation timing is supported by the lack of ore MVT ore deposits within structures such as the Alyn Valley Fault in the Vale of Clwyd that have been attributed to the post-Carboniferous phase of extension (Davies et al., 2004).

Uplift continued into the Jurassic, followed by reburial. The reactivation of faults during this time could have allowed surface derived marine/meteoric and/or formation fluids from the overlying siliciclastic units
to percolate and interact with fluids that may have been derived within the Permo-Triassic and Jurassic basin formations. These fluids were likely to carry elements required for mineralisation (copper and minor galena) that cross-cut the earlier MVT deposits. Moreover, this is consistent with trace element release related to hydrocarbon maturation (Floodpage, 2001) and the dissolution of detrital minerals during burial. The introduction of surface derived fluids could account for dedolomitisation and later calcite cements that occlude the remaining secondary dissolution enhanced porosity.

8.6 Comparison with other UK, age equivalent carbonate platforms

A number of age-equivalent carbonate platforms were established during a period of extension in the UK. These include the South Wales, Derbyshire, Askrigg and Alston Platforms, and the Isle of Man. Moreover, they have all been subjected to burial and multiple episodes of structural deformation to varying degrees.

The main stage fault and fracture related mineralisation took place during the waning stages of extension and the onset of the Variscan Orogeny. Trace elements were released during organic maturation (Floodpage, 2001). Temperatures reached >90°C and minor hydrocarbon generation within the East Irish Sea Basin occurred in the Namurian-Westphalian. This limited the trace elements available during mineralisation and cementation. The main phase of hydrocarbon generation and maximum burial took place during the Jurassic (Floodpage, 2001). Much of the hydrocarbon was retained within structural traps within the basin.

In comparison, the Derbyshire Platform hosts larger volumes of mineralisation and although insignificant, more hydrocarbon than the North Wales Platform. Early dolomitisation although related to faulting and fracturing was sourced from basin sediments (Hollis, 1996; Hollis & Walkden, 2012). A geothermal gradient of 30°C km⁻¹ occurred in the Widmerpool and Staffordshire Basins (Russell, 1992), which is the same
as that suggested for the North Wales Platform (Al-Fadel, 1983; Floodpage, 2001).

Similarly to the North Wale Platform, the southern margin of the Askrigg Platform hosts lower volumes of mineralisation than the Derbyshire Platform (e.g. fluorite). However, it has been suggested that The Craven Basin was subject to an elevated geothermal gradient (50°C km\(^{-1}\)) (Plant & Jones, 1989; Hollis, 1998) hydrocarbon generation and clay diagenesis was complete prior to the onset of the Variscan Orogeny (Hollis, 1996).

The platforms experienced similar early diagenetic histories and the main difference occurred during contrasting burial histories. The main differences are a result of: fault fracture systems, availability of trace elements, organic matter maturation, fluid leaking or trapping (Hollis, 1996; this study).

**Europe**

Comparative dolomitisation and mineralisation deposits hosted by Palaeozoic carbonates and situated on the periphery of the Variscan Orogeny have been recorded across Europe. These include Ireland Midlands (Wright et al., 1999; Shelton et al., 2012), Spain (Gasparrini, 2003), Belgium (Nielsen et al., 1998). These deposits share similar petrographical, geochemical, and geometrical characteristics. Moreover, they are commonly related to fault and fluid circulation. However, timing is considered to be later than the UK examples, and potentially occurred during a period of extension in the Permian (Gasparrini, 2003). This is considered to be a time of fluid migration subsequent to the Variscan Uplift that has been recognised throughout Western Europe (Schneider, 2000).

**8.7 Implications for hydrocarbon exploration and production**

As detailed in the introduction combined sedimentological, diagenetic and structural studies are vital to understanding fluid storage and flow within carbonate reservoirs (see chapter 1). The results presented within this
study are considered relevant to hydrocarbon production in terms of understanding porosity characteristics evolution within platform carbonates.

Porosity within platform carbonates is intimately linked with the depositional, structural and diagenetic history. Primary porosity reflects depositional facies, providing an abundance of fenestral, intra and interparticle porosity. Following deposition porosity can be altered and occluded by diagenetic products such as compaction and cementation; this can occur into deep burial and hinder fluid and hydrocarbon flow. Conversely, porosity can also be developed during burial through dissolution and leaching.

The North Wales Platform, although in close proximity to the hydrocarbon producing East Irish Sea Basin, does not possess favourable reservoir characteristics. The limestone became well cemented early in its diagenetic history, which occluded the majority of the primary porosity. Secondary porosity in the form of faults, fractures and dissolution voids have also largely been occluded by multiple fluid flow events that were linked to the structural evolution of the region.

Although diagenetic outcrop studies can greatly aid in understanding the porosity evolution within other ancient systems current-day observations cannot be directly applied. At present, producing reservoirs are buried for up to several kilometres where the physio-chemical and therefore controls on porosity are different from exposed limestone. Diagenetic study including the study of the size, shape and distribution of diagenetic products such as dolomite bodies and cements can help us understand the conditions at a single point in the geological history. Understanding how those conditions changed trough time can help us understand carbonate systems that have been subjected to similar burial histories. This is method has become common practice within geological and reservoir evaluation as we can use the knowledge for prediction of the connectivity and heterogeneity of porosity and permeability in carbonate rocks.
8.8 Future work

Lower Carboniferous outcrops including the North Wales Platform provide unique datasets that can provide a greater understanding of diagenetic processes and patterns within carbonate platforms. This is important especially when dealing with subsurface data. However, there are still several issues surrounding different aspects of diagenesis and beyond the scope of this study. The issues specific to this study are outlined below, these need to be investigated in order to fully understand the North Wales Platform and exploit the dataset.

The most important outstanding uncertainty is the composition of the fluids responsible for the MVT mineralisation in North Wales. Isotopic, geochemical petrographic analysis can offer an insight into the composition but reactions and overprinting alter the original composition. The best way to determine the original fluid composition is combining fluid inclusion data with the standard techniques. This analysis requires a large quantity of primary fluid inclusions, of which were lacking within the polished sections. It is suggested a larger petrographic dataset may overcome this issue. In addition, non-conventional isotope systems sulphur, Mg and isotope clumping techniques although not new have made new advances in the past few years (e.g. Eiler, 2007). These techniques may provide useful tools to characterisation of cements and constraint on the source of diagenetic fluids. This will be especially effective where overprinting by successive diagenetic phases produce complex cross-cutting relationships.

Determining the burial history across the North Wales Platform with confidence is problematic. The difficulty lies within the estimating the amount of sediment removal from the area and the variable subsidence related to faulting. More detailed and well conditioned modelling is therefore suggested for the North wale Platform.

Dating of the mineral deposits still remains debatable. The paragenesis provides a framework and a relative timing of the mineralisation in relation
to structure and cements. However, this does not provide a definite age. Pb-Pb techniques, although potentially unreliable, may improve the evaluation through a larger dataset. K-Ar analysis could be employed to the mineralisation and contemporaneous gangue cements providing a potentially more accurate dating technique.

Lastly, further work is needed in order to fully test the potential for fluid flow within this geological and structural evolution. This is possible using forward modelling. This would add further constraint to the timing, source and volumes of fluid responsible for cementation on the platform.
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