THE SEDIMENTOLOGY AND DIAGENESIS OF THE

PENDLESIDE LIMESTONE GROUP IN THE

CRAVEN BASIN OF NORTHERN ENGLAND

VOLUME I

A Thesis Submitted by

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For The Degree of

DOCTOR OF PHILOSOPHY

The University of Aston in Birmingham   October, 1979

Dedication

To my mother and my late father

THANKS BE TO GOD, THE ALMIGHTY
THE MOTHER WHO FED ME
THE FATHER WHO CLOTHED ME
THE TEACHER WHO TAUGHT ME
AND THE WOMAN THAT INSPIRED ME

ACKNOWLEDGEMENTS

Farid Arsen Iskenderian   Ph.D.   1979

SUMMARY

This thesis describes the stratigraphy, sedimentology and diagenesis of the Pendleside Limestone (Asbian age), a sequence of limestones, shales and dolostones in the Clitheroe area of N.W. England. Field study of 19 measured sections indicates that it was deposited in a rhythmically subsiding basin (Craven Basin) because of movements on the Mid-Craven Fault which was active in Dinantian times. The sequence is up to 190 m thick and consists mostly of distal turbidite deposits which have been reworked at horizons when sediment accumulation built up to the wave base.

The original depositional fabric and mineralogy of the Pendleside Limestone Group has been extensively modified by diagenetic processes including cementation, authigenesis, dolomitization and silicification. These processes have been studied using a wide variety of laboratory techniques. The carbonate cements of the Pendleside Limestone consist predominantly of ferroan calcite and non-ferroan calcite with microdolomite inclusions. The former is probably a stable replacement of original-high-magnesian calcite. Cementation was accompanied by the formation of authigenic albite and quartz.

Much of the upper part of the Pendleside Limestone has been extensively dolomitized and chertified. Several distinct zones of dolomitization are found which increase in thickness and intensity towards the top of the Pendleside Limestone Group. The dolostone horizons correspond to coarser-grained lithologies deposited during periods of shallow water sedimentation. The composition of the dolomites changes from ferroan dolomite in the lower part of the Group to non-ferroan dolomite in the upper part. The low strontium and sodium content of the dolostones in association with the other evidence suggests that the dolomitization was brought about in an open system by the mixing of marine and fresh water in phreatic lens which were established at periodic intervals. The dolomitization was closely associated with chertification although this was initiated by the dissolution of siliceous spicules which provided the necessary source of silica.

CARBONIFEROUS, LIMESTONES, DIAGENESIS, DOLOMITIZATION, CHERTIFICATION

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PART I

STRATIGRAPHY AND SEDIMENTATION

Chapter One

INTRODUCTION

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INTRODUCTION

1.1   The Dinantian in Britain

The Lower Carboniferous rocks in Britain were deposited along the margins of an inferred landmass (the Atlantean Continent) to the south of which four major depositional provinces were separated by upwarps that defined an archipelagic environment, and that formed barriers between individual provinces, whose isolation is reflected in contrasts of stratigraphical sequence (George, 1971) (Fig. 1.1).

The southwestern province covers South Wales and southern England. The deposits show in full Dinantian sequence a consistent southward replacement of coral-brachiopod shelf limestones (Carboniferous Limestone) by goniatite-lamellibranch shales and cherts. Northwards there lies a major upwarp (St. George's Land) towards which the sediments become increasingly sandy and thin both by overlap and by overstep.

St. George's Land was an effective barrier to the north of which the Central Province displays a variant sequence mainly of Carboniferous Limestone. Tournaisian beds are not widely recognizable in it and are absent over much of it; but Visean beds include thick development of shelf limestones (with reefs) and rocks of so-called basin facies characterized by goniatite shales. The zonal schemes established by Garwood (1907, 1913) in the limestones and by Bisat (1928, 1952) in the shales thus diverge from the prototype zonal scheme established by Vaughan (1905) in the South Western Province.

The Scottish Province lies beyond the Southern Uplands Massif. In it the sedimentary sequence is interrupted by great thicknesses of lava, notably the Clyde Plateau lava in the

lee of which lagoonal oil shales accumulated. Most of the Scottish rocks are deltaic
terrigenes of a variety of kinds, some give evidence of brackish water conditions, and
only a comparatively small proportion are typically marine. As in Northumbria a zonal
sequence is difficult to establish and later Visean sediments alone have been satisfactorily
dated (George, 1967).

The Central Province   defined by the complex upwarp of the Manx-Cumbrian
ridge and the Askrigg and Alston Blocks, the general effectiveness of which as a barrier is
shown by the major contrasts between the Carboniferous Limestone of the Central Province
and the sediments of the Northumbrian Province, which in large part are terrigenous and
deltaic in Yoredale rhythms. A standard zonal sequence cannot therefore readily be
established, and only upper Visean sediments are at all confidently correlated with their
equivalents farther south: most of the earlier rocks are not typically marine (George, 1967).

1.2   The Asbian stage

The Dinantian subsystem in Britain is divided into six Stages:(George et al·1976)

Brigantian

Asbian

Holkerian

Arundian

Chadian

Courceyan

Rocks of the Asbian Stage represent a particularly wide range of facies, especially between
block and basin areas. The rocks between the massif of North Derbyshire and the Askrigg
Block comprise mostly dark bituminous limestones and mudstones, together with some
turbiditic sandstones and limestones which have entered the area from the north. The rocks

are best known in the north of the district, but the rocks of the boring at Alport (Hudson

and Cotton, 1945) just to the north of the Derbyshire limestone outcrop, are also basinal,

though nothing is known of the Dinantian rocks at depth between Alport and the Clitheroe

district.(Fig 1·2).

To the north of the Clitheroe district, the belt of reefs between Settle and Malham,

forming a marginal facies between the Askrigg Block and the Craven Lowlands, are mainly

of Asbian age, some of them continuing upwards from the Holkerian (Hudson and Mitchell,

1937; Hudson and Dunnington, 1945; Hudson, 1949). The reefs contain characteristic

brachiopods, goniatites and trilobites. In the basin the beds include the turbiditic

Draughton and Pendleside Limestones, which contain few underived fossils.

1.3   The Pendleside Limestone Group

Not much work has been accomplished regarding the sedimentation and diagenesis

of the Pendleside Limestone Group. Most of the accomplished work on the Dinantian

describes the palaeogeography, lithology and stratigraphy of the Craven Basin. Few

people discussed the environment of deposition of these strata or the diagenetic processes

involved and the products thereof.

Hind et al. (1901) described the Lower Carboniferous succession and referred to the

Pendleside Limestone Group. They described the Pendleside Limestone sequence on Pendle

Hill and grouped it into limestone-shale horizons with their associated cherts. They

described the limestones as hard, black, very compact and close-grained with a sub-

conchoidal fracture, fossiliferous in some horizons. They also referred to the dolomitization

of the Pendleside Limestone but there have been few recent studies of dolomitization in

basinal limestone successions, especially in the Craven Basin.

Other work was accomplished by Parkinson (1935). He referred to the tectonics and stratigraphical sequence of the Pendleside Limestone Group in the Slaidburn area.

Earp et al. (1961) described the Pendleside Limestone Group during the geological survey of the area. They described the beds as strong cementstones with subsidiary shale partings. The limestones are dark grey, hard, compact and fossiliferous in some parts. They also referred to the dolomitization and silicification of the limestones in the upper part of the succession. They defined the lower part of the Pendleside Limestone Group at the base of the B. hodderense Beds, whereas the top is defined at the base of the Bowland shales.

Many problems exist regarding the origin of sediments, sedimentation, and the mechanisms controlling the sedimentation of the Dinantian in the Craven Basin. Ramsbottom (1973) proposed that eustatic sea level change was the main controlling mechanism of sedimentation of the Carboniferous in the Craven Basin. He assigned the sedimentation of the Six Major Cycles (which he distinguished and classified) to a universal change in sea level which brought about the transgression and regression of the Carboniferous sea, thus influencing the deposition in the Craven Basin. George (1978) rejected the eustatic sea level change proposed by Ramsbottom (1973). He proposed that the tectonic activity was the controlling mechanism of the Carboniferous cyclic sedimentation. He provided evidence against Ramsbottom's theory of eustatic sea level change and advanced evidence confirming his theory of the tectonic origin. George (1978) regarded the subsidence of the sea floor as the main mechanism for the Carboniferous sedimentation. Both theories are discussed in subsequent chapters.

The work involved in this project is classified into two parts. The first part describes the stratigraphy and sedimentation of the Pendleside Limestone Group. The stratigraphy

involves the identification of the major facies and the faunal assemblage which verify the age and environment of deposition of the Pendleside Limestone Group. The sedimentation is complementary to the stratigraphy; it includes a description of the depositional environment of the Pendleside Limestone Group, and shows how the main facies variations can be explained in terms of variation in the depositional environment. The second part of this work involves diagenesis and authigenesis. The diagenetic processes that the Pendleside Limestone has undergone influence a great deal in the creation of new fabric, neomorphism and other diagenetic features. Processes such as dissolution, cementation, replacement and pseudomorphism are all discussed in this part of the thesis. Dolomitization and chertification are the major diagenetic processes involved in the diagenesis of the Pendleside Limestone group. These are discussed in detail and in conjunction with the literature.

A wide variety of geological techniques have been used in this study of the Pendleside Limestone Group. Available sections have been logged and sampled in detail. All samples have been subjected to routine X-ray diffraction analysis and stained thin sections have been made of all the samples. Selected material has been studied using scanning electron microscopy (SEM) and electron probe microanalysis. A large number of samples have been analysed using atomic absorption spectrophotometry. The author has been personally responsible for all the preparation and analysis using these techniques.

Chapter Two

STRATIGRAPHY

2.1   Introduction

2.2   The structure and stratigraphy of the Craven Basin

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Chapter Two

STRATIGRAPHY

2.1 Introduction

This chapter involves a review of the Dinantian stratigraphy and application of proposed stratigraphical schemes to the Craven Basin.

One of the earliest events that triggered the interest in the geology of the Yorkshire area was the visit of the Belgian geologist Lohest to Yorkshire in 1886. His work together with de Koninck (Ramsbottom et al., 1974), led them to believe from the palaeontological evidence that only the upper part of the Belgian sequence was present in Yorkshire. We now know that Tourn.aisian beds are represented in Ravenstonedale and the Craven lowlands (Ramsbottom et al., 1974).

Garwood and Marr (1895) made further observations on zones in Yorkshire and Northumberland which were to lead to Garwood's preliminary zonal scheme of 1907, and his final zonation of 1913 in which a correlation with Vaughan's (1905) zones in the Bristol area was given. Although there were always difficulties in correlation of the southwestern, and northern England provinces, these were analysed by Hudson and Dunnington (1945) who were able to give a distinctive meaning to some of Vaughan's zonal symbols, i.e. (lower Caninia) C_1 and (upper Caninia) C_2, when used in Yorkshire.

The major problem in applying Vaughan's (1905) zonal scheme, as was shown by Mitchell (1972) and Ramsbottom (1973), is that the Bristol succession conceals four substantial non-sequences in the Viséan rocks, which are represented by substantial stratigraphic thickness in the north of England succession.

Some of the previous schemes of zonal classification of the Carboniferous

Limestone are illustrated in Fig. 2.1, where Vaughan's zones of the southwestern

England are compared with Garwood's zonal system of Yorkshire. Both systems are

correlated with Hudson's zones which are based on goniatites, and Cumming's zonation

based upon the foraminiferal assemblage (George, 1969).

The formal and most accepted classification of the Carboniferous is that established

by Ramsbottom (1973), and George et al. (1976). They described and classified the beds

in the lower Carboniferous into six cycles of sedimentation (Ramsbottom, 1973), four of

which are major eustatic cycles of transgressions and regressions up to the D_1 (Dibuno-

phyllum) zone, the remaining two cycles being divided into minor transgressions and

regressions as shown in Fig. 2.2, for three Carboniferous provinces. These cycles of

sedimentation were subsequently used as the basis for the divisions of the Dinantian into

six stages (Chapter1).

Ramsbottom (1973) defined the transgressive phases of each cycle by bioclastic

limestones or calcareous shales, and the regressive phases by the presence of ooliths or

calcite mudstones, and by stromatolitic and nodular algae, or at some levels by sand-

stones or reef-knolls. He described the calcite mudstones and associated rocks of the

regressive phases as often showing signs of desiccation and dolomitization.

Ramsbottom (1973) believed that the dolomitization and desiccation was due to the

effects of hypersalinity caused by the partial regression of the sea from the shallow shelf

regions. Naturally beds just below the regressive phase are also dolomitized by the

downwards percolation of the magnesium-rich waters of high salinity produced during

times of desiccation.

The beds of the first major cycle of Ramsbottom (1973) are assigned to the

Tournaisian, they occur in two basinal areas of the Craven lowlands (Figs. 2.3, 2.4) and Ravenstonedale. The beds of the transgressive phase are dark, well bedded, bituminus limestones and calcareous shales of typical basinal type, whereas the regressive phase of this first cycle is seen in the oncolitic algal nodules (Solenpora) and some dolomitic rocks. The beds of the second major cycle show marked variation in thickness. For example, to the east of Clitheroe and towards the area around Skipton cycle 2 beds are almost absent, whereas in the west and southwest they show a full succession. Ramsbottom (1973) argued that this may be due to unconformity which is more pronounced towards the east or that the beds of the upper part of the cycle were never deposited.

On any account, the lowest beds of the second major cycle are mainly dark bioclastic limestones of basinal type, with some subsidiary shales. Some of the dark grey or black, strongly bituminous limestones show graded bedding and sole markings; also fossils are scarce and there are many interbedded shales. Many of these beds are probably turbiditic limestones.

The regressive phase of cycle two in the Craven Basin is represented by the thick series of beds which include knoll-forming lime-bank deposits. The cores of the reef-knolls are formed of poorly-bedded calcite mudstones (the bank facies) with an abundant and specialized fauna dominated by certain brachiopods, mollucs, and fenestellid bryozoa. Miller and Grayson (1972) recognised flank and interbank facies, both usually rich in crinoids. Resting on the bank deposits there are in many places boulder beds and breccias (Hudson, 1927; Miller and Grayson, 1972) overlain either by crinoidal lime-stones (Salt Hill Cap Beds) or by dark shales (Cephalopod Shales) of the next cycle. The origin of these reef-knolls has been debated for many years (Ramsbottom et al., 1974).

Tiddeman's theory (1889) which was reinforced by Parkinson (1968), envisaged

primary accumulations of biogenic deposits growing on a sinking sea floor, with quaquaversal dips; the contemporary breccias indicated that the mounds were soon lithified and were partly wave resistant.

Earp et al. (1961) considered that binding organisms were lacking, the breccias not contemporaneous, and the dips compactional; accordingly the structures were not considered as wave-resistant but lime-bank deposits.

Miller and Grayson (1972) believed that bank facies formed as sheets and mound-like lime-banks with depositional dips. They presented evidence of lithification and subaerial erosion of the reef-knolls prior to the deposition of Cycle 3.

Ramsbottom (1973) described the transgressive phase of the third major cycle as a substantial one, just as the regressive phase of the second major cycle which was an extensive phase throughout the Dinantian. The beds representing the transgressive phase of the third major cycle over the Askrigg Block area, are the thin development of the Michelinia grandis Beds of Garwood which are generally grey and dark grey, richly fossiliferous and often cross-stratified bioclastic limestones. He described the lowest beds as containing pebbles of limestone and other lower Palaeozoic rocks, the beds resting unconformably on the folded lower Palaeozoic basement. In the Craven lowlands the facies are quite different being considerably more argillaceous than the Michelinia grandis Beds and less fossiliferous. The limestones also show slumping (Embsay Limestone and Broughton Limestone) (Dunnington, 1945), and contain limestone pebble beds at their base.

Being basinal sediments, the proportion of shale increases southwards towards the centre of the basin; and the limestones decrease in thickness in the generally shaly sequence.

The regressive phase on the southern part of the Askigg Block and around Ravenstonedale is represented by dolomitic, sparsely fossiliferous limestones and by the presence of sandstones (Ashfell Sandstone). The shallowness of the water is further indicated by the algae of the Gastropod beds.

The Fourth Major Cycle contains bioclastic limestone in the transgressive phase comprising, pale grey, rather thin-bedded calcarenites and micrites. The exposures at the lower part of the sequence in some places show minor cyclicity – thin beds of sandstone and shale interbedded with fining-upwards limestones, whereas in the higher part of the sequence, the cyclicity is absent although there are several sandstone and shale layers. The sequence has various names in different localities; for example in the Stainmore Trough it is called the Hillbeck Limestones. The limestones of the transgressive phase on the Askrigg Block thicken northwards and trangress on to the Lower Palaeozoic rocks, whereas in the south, especially in the Settle district the lower part is thought to be missing. For the most part, the limestone of this cycle is distinctly unfossiliferous, though crinoids are locally abundant.

In the southwest part of the Askrigg Block, where the lowest D_1 (Lower Dibunophyllum) beds are missing, the top part of the S_2 (Upper Seminula) zone is dolomitized, one result of this local unconformity at the cycle boundary.

The regressive phase of the Fourth Major Cycle is represented on the Askrigg Block by the Porcellaneous Beds, pale white-weathering calcilutites showing some desiccation cracking and occasional stromatolitic layers.

The Fifth Group of Minor Cycles (D_1 zone) shows considerable facies variation. The lowest beds of the (D_1) transgression occur only in the Stainmore Trough. They are mostly dark grey limestones showing minor cyclicity and with burrowed hardgrounds.

It was only later that the transgression reached on the southern Askrigg Block and the Alston Block, and in these areas there is thus a nonsequence at the base of D_1 with the former beds of D. Llangollensis. This would suggest that there was an upward tilting of the southern edge of the Askrigg Block which was already taking place in early D_1 times.

The beds on the Askrigg Block and along the Southern margin are mostly rather thick-bedded, pale grey calcarenites (Great Scar Limestone), and are characterized by prominent master bedding planes.

The indications that D_1 limestones were formed in shallow waters are that the shale beds often rest on an uneven hummocky limestone surface and sometimes appear to be filling grike-like depressions. These uneven surfaces are probably palaeo-karstic surfaces like these described from Derbyshire (Stevenson and Gaunt, 1971). Other indications of shallow water environment are the coal and carbonaceous laminae that occur at several horizons in the D_1 beds and also the pseudobreccias, the "spotted beds", and "stick beds" of Garwood (1913). These are a conspicuous characteristic of the D_1 limestones. There has been much speculation about the origin of these pseudobreccias. Grayson (in Ramsbottom et al., 1974) suggested that these are caused by bioturbation, but there are all gradations between the clearly burrowed "stick beds" of Garwood and the less obviously burrowed pseudobreccias. These pseudobreccias in the southern Askrigg Block are commonest in the higher beds of the zone, but to the north they occur in the lower beds. These pseudobreccias could represent the collapse of soft calcareous sediments following the compaction failure of a stabilizing (algal?) crust. In the north, on the Alston Block and in the Stainmore Trough, the minor cycles in the upper D_1 beds are of Yoredale facies.

Ramsbottom (1973) discussed the reef-belt in the country immediately to the south

of the Mid-Craven Fault and at the southern margin of the block. The shelf calcarenites of the southern margin passes southwards into distinctive types of limestone - the knoll reefs and their associated bedded limestones. Three main theories have been proposed as regarding the origin of the knoll-reefs. First, Tiddeman (1889) believed that the reefs grew as mound-like accumulations on a sinking sea floor from the debris of the animals which grew there.

Secondly, Hudson (1930) argued that the continuous belt of reef limestones along the southern margin of the Askrigg Block developed as a southerly facing reef-apron which was faulted and eroded into knoll-like forms before the deposition of the Bowland Shales (Fig. 2.3).

Thirdly, Black (1958) who originally suggested the occurrence of pre-Bowland Shale faulting and folding, mentioned that in addition to a reef-apron at the edge of the massif, independent knoll-reefs grew on the sea floor immediately to the south, and, according to Black, such faulting as occurred took place during late P_2 (upper _Posidonia_) or early E_1 (Lower _Eumorphoceras_) times, as shown by the presence of boulder beds in the Bowland Shales.

Hudson (1930) again concluded that the lowest beds of the reefs in two localities Scaleber and Cracoe were of upper S_2 (upper Seminula) age. This bears out the hypothesis that the growth of the reefs began during periods of regression at the end of the Fourth Major Cycle. The growth must thereafter have kept pace with the changes in sea level throughout the D_1 zone. This is indicated by the fauna of the upper beds of the knolls which contain, along with abundant molluscs, brachiopods and fenestelloids. The cessation of reef growth thus coincides with the widespread facies change at the base of D_2.

In the Craven lowlands the deposits of this age in the basinal area are quite different from the thick-bedded calcarenites of the Askrigg Block being composed principally of shales or mudstones with subsidiary limestones. The base has not been placed in this shaly succession, but the palaeontological evidence (Ramsbottom et al., 1974) suggests that it occurs in the Cephalopod Shales, some distance below the Bollandoceras hodderense Beds which are a marker horizon consisting of spotted calcitic mudstones.

In the area around Clitheroe and further south, the D_1 beds comprise a lower group of shales and thin limestones, including the B. hodderense Beds and an upper group of limestones and dolostones, the Pendleside Limestone. The lowermost beds of the overlying Bowland Shale Group are also considered to be Asbian in age, whilst the main part including the Pendleside Sandstone, is of Brigantian age (George et al., 1976). Many of these D_1 limestone-shale sequences show turbiditic features, which are especially well-displayed in the Hodder River section (S.100).

In the area around Skipton and Rylstone the thickness is much less and the equivalent of the Pendleside Limestone is called the Draughton Limestone which is only about 30 metres thick. The Draughton Limestone contains numerous limestone conglomerate and breccia horizons, some showing graded bedding, and is thought to be a proximal turbidite sequence (Ramsbottom et al., 1974). The Pendleside Limestone is thought to be a distal equivalent. Detailed correlation is precluded because of the pre-Bowland Shale erosion.

Hind et al. (1901) gave an account on the Lower Carboniferous succession in between the "Mountain Limestone" and the Millstone Grit and referred to the Pendleside Limestone Group. They described the Pendleside Limestone sequence on Pendle Hill and

grouped it into limestone horizons with their associated cherts that are of two types: a pale light grey, white weathering rock, and a black compact rock with ill-defined spongy material. They described the limestones as hard, black, very compact and close-grained with a sub-conchoidal fracture, fossiliferous in some horizons. The fossils are foraminifera, bryozoa, hydrozoa, sponges, crinoids and occasional fragments of brachiopod shells.

Hind et al. (1901) also referred to the dolomitization and noted that some of the dolomite rhombs are well-developed and stained or rimmed with iron oxide and in the silicified horizons the rhombs are inconspicuous or ill-defined bodies floating in the silica matrix.

Ramsbottom (1973) divided the Sixth Group of Minor Cycles into two distinct facies:

i) The Yoredale facies, north of the Craven Faults, which extend from the base of the D_2 (Middle Dibunophyllum) zone to the base of the Namurian. The deposits are strongly cyclic, with repetitions of limestone, shales, sandstones and thin coal. In general, Ramsbottom (1973) described the sandstones and the shales to thin southwards and southeastwards very considerably, especially in the lower part of the sequence, so that the lower beds in the south are limestones with a few thin shale beds. Also there is less thinning of the limestones to the south in the southern region of the Askrigg Block especially in the upper beds. The thickness as a whole shows that the influence of the Stainmore Trough was still strong at the time, even though there were no facies changes across it, apart from the clastic beds which have thickened in the trough.

The reasons for the southward thinning of the sandstones and shales is that as we go to the south the distance increases from the source of input of the deposits, which is

in the north, and in addition there was the uplift along the southern edge of the Askrigg

Block together with accompanying contemporary movement of the Middle Craven Fault.

There are notable indications of an unconformity developed regionally by the change

in lithology in some areas and in faunal assemblege and distribution as stated by

Ramsbottom (1973).

The Yoredale facies is now known to be of deltaic origin (Moor, 1958) and the

cyclicity can be considered to be due to a combination of subsidence and delta-switching

on a marine platform.

The most recent studies of the Yoredale Facies were carried out by Elliot (1974).

Elliot (1975) discussed the morphology, magnitude and regime of the Carboniferous

(Yoredale) delta lobe. He assigned the Carboniferous (Yoredale) delta lobe to the

meandering fluvial distributary which was initiated into the interdistributary bay by

avulsion. He gave an account of the sedimentological history of the delta lobe from

the Yoredale Carboniferous cyclotherm (Elliot, 1976) and divided the complex history of

sedimentation into four distinct phases 1) the coastal plane phase 2) progradational

phase 3) abandonment phase 4) post-abandonment phase. He described the Abandonment

Facies of High-constructive Lobate Deltas from the Yoredale series as destructive phase

of sedimentation which followed the abandonment of the lobe and produced thin, but a

distinct stratigraphic marker horizon of variable facies.

ii) The Bowland Shale Facies: which are divided into: The Visean part of the

sequence, known as the Lower Bowland Shales, which consist of mudstone and shales,

and the Namurian part of the sequence, known as the Upper Bowland Shales (Ramsbottom,

1973). These facies are characteristic of the Craven Basin.

A)   The Lower Bowland Shales are dark grey to black mudstones and shales, usually calcareous and characterized by a non-benthic fauna of goniatites and swimming bivalves, spiriferoids and chonetoids. These shales contain calcareous nodules which contain uncrushed fossils and are known locally as bullions. The Lower Bowland Shales rest unconformably on top of the Pendleside Limestone Group.

B)   The upper part of the Bowland Shales, especially in the Pendle Hill area, consist of a series of sandstones known as the Pendleside Sandstone which correspond roughly to the Nettleber Sandstone of the Skipton area. It also corresponds to the thickest and most persistant sandstones of Yoredale Facies to the south.

It is argued that the Pendleside Sandstone is derived from a northerly source because of its mineralogical and lithological components, which are feldspathic and contain some turbiditic beds.

2.2   The structure and stratigraphy of the Craven Basin

One of the major structures in the Craven Basin is the northeast-southwest folding of the Ribblesdale Fold Belt. This belt, described by Hudson (1937) is, however, far from being a simple structure since it is crossed by fault systems, known as the Clitheroe, Rimington, Barnoldswick and South Craven Faults, which run approximately northwest-southeast, down through to the south, and have considerable lateral shift, thus dividing the fold belt into four major structures, the Clitheroe, Middop, Thornton, and Skipton Anticlines, each plunging to the northeast (Fig. 2.4).

The Thornton Anticline extends from the Barnoldswick Fault to the South Craven Faults with its southern flank dipping steeply to the Carleton Syncline (Hudson and

Mitchell, 1937), the general dip being about 70°. The northern flank has, in general, a much less steep dip and the various beds have much wider outcrops. A strong strike fault, the Bracewell-Broughton Fault, extends along the anticline oblique to its axis and with a downthrow to the south separating the plunging end of the anticline from the main structure; it is the isolated part of the anticline north of the Bracewell-Broughton Fault which is known as the Broughton Anticline. This anticline is crossed by the Coniston-Cold Fault, a branch of the South Craven Fault, and it is separated from the Skipton Anticline to the east by the Gargrave Fault, another branch of the same fault system (Fig. 2.4).

Many authors have discussed the geology of these anticlinal fault blocks, such as Hudson and Mitchell (1937), who discussed the geology of the Skipton Anticline. The Dinantian succession here is 1000 m thick, consisting of mudstone, shales, and dark grey argillaceous limestones in varying proportions. At three levels, the limestone is more abundant than shale, these limestone beds are distinguished as the Haw Bank Limestone, the Embsay Limestone, and the Draughton Limestone, and the beds between the two former as the Halton shales-with-limestones and between the two latter as the Skibeden shales-with-limestones (Fig. 2.5). Above the Draughton Limestone and Shales, a series of mudstone and shales with thin limestones is gradually replaced by shales with limestone nodules. These pass into ferruginous and micaceous shales, becoming more sandy upwards and are finally succeeded by the coarse sandstones and pebbly grits of the Millstone Grit.

Hudson and Dunnington (1944) discussed the lithology and stratigraphical sequence in the Swinden Anticline and described the beds in the main part of the Swinden Anticline as mainly evenly bedded, dark grey limestones, and calcareous shales. They described the limestones as finely detrital and usually with abundant foraminifera. They mentioned

that the beds are often dolomitic and occasionally cherty. As for the lower part of the

succession they described the limestones as light coloured, not well-bedded and poorly

fossiliferous and in one part of the Swinden Moor area they pass into non-bedded light

coloured reef-limestones with shaly-reef fauna. The shales they described as usually

coarse, unfossiliferous, and containing thin limestones.

Hudson (1944) described the Broughton Anticline which is similar to the Thornton

Anticline, he described ⟨ the succession ⟩ as mudstones, shale, and dark grey argillaceous and sometimes

dolomitic limestones in varying proportions, no reef-limestones are present. The lower

group of beds is the Haw Bank Limestone above and the Haw Bank limestone - with

shales below. Above the Haw Bank beds, the beds consist of shales with limestones

below followed by a limestone series above; these are called the Thornton Beds. They

are followed by the Butterhaw Shales with Limestones below and the Butterhaw Limestones

above. On the top of the Butterhaw Beds, which are separated by an unconformity, lies

the Skibeden Shale with limestones.

Parkinson (1935) has provided the most recent description of the stratigraphy

and tectonics in the Slaidburn area. The main features of the area are two

northeast-southwest trending anticlines, the Slaidburn and Sykes anticlines (Fig. 2.4).

These are transected by a northwest-southeast trending system of faults, the Clitheroe

fault system.

The succession within these anticlines is quite different from that in the Clitheroe

area and Parkinson (1935) distinguished five lithological groups:

a) The Clitheroe Limestone, which he couldn't subdivide in the same manner as

in the Clitheroe area because the reefs enter at a higher horizon and terminate at

lower horizons than in the Clitheroe area. He divided the Clitheroe Limestone in the

Slaidburn area on the basis of the occurrence of Caninia into two stratigraphic zones, upper and lower Caninia zones.

b)   The Worston Series, which Parkinson (1935) described as variable in thickness and predominantly argillaceous in the south to predominantly calcareous in the north. The change in lithology reflects a change in the type of fauna.

c)   The Pendleside Limestone Series, which Parkinson (1935) defined as the strata from the B. hodderense Band to the base of the Lower Posidonia zone. He described the beds as much thinner than in the type area of Pendle Hill and in places   completely absent. They frequently consist of limestone breccias which unconformably overlie finer grained bioclastic limestones with thin shales.

d)   The Lower Bowland Shales, which he subdivided into Lower Posidonia and Upper Posidonia zones. He described the beds as consisting mainly of mudstones and shales.

e)   The Upper Bowland Shales and Namurian Grit: Parkinson (1935) described the rocks of this series as dominantly black shales which had a constant thickness throughout the Craven lowlands. He described the lithology as varying in different beds from argillaceous to calcareous.

A remarkable feature of the different anticlinal blocks in the Craven Basin is the manner in which they control the spatial distribution of the depositional facies. This is well-illustrated by the Pendleside Limestone Group.

In the Clitheroe Anticline the thickness of the Pendleside Limestone is 150 metres and the lithology comprises an alteration of shales with limestones, predominantly fine grained micrites and peloidal biosparites, dolomitized in places. In the Thornton Anticline the Pendleside limestones consist mostly of spiculitic micrites, whereas in the Slaidburn Anticline the Pendleside Limestone is 35 metres in thickness and consists of limestone breccias and conglomerates unconformably overlying bioclastic limestones

/hich are dolomitized and silicified in places.

!.3   The Geology of the Pendleside Limestone Group in the area

around Clitheroe

The study area of this project covers the area around Clitheroe, sheet 68 of the Geological Survey of Great Britain, between long. 2°.25' – 2°.50' west and lat. 53°.50' – 53°.55' north.   Outcrops of the Pendleside Limestone Group are differentially exposed in different anticlinal blocks. Some of the exposures are fully representative of the Pendleside Limestone Group. These include three sections on Pendle Hill at Rad Brook and sections 400 and 500, and also in the Hodder River section (100) in which the Pendleside Limestone displays a full succession throughout the outcrop. The outcrop pattern and location of the studied sections are shown in Fig. 2.6.

The Pendleside Limestone Group is described on a lithostratigraphical basis in each locality. On Pendle Hill, which is the type locality for the Pendleside Limestone Group, the succession attains a thickness of 144 metres. The Group base is defined at the beginning of the Bollandoceras hodderense Beds, which is an important marker horizon in the Clitheroe area. The top of the Group is marked on Pendle Hill at the base of the overlying Bowland Shale Group.

Seven sections have been logged and sampled in the Pendle Hill area, three of which, Rad Brook (788428) which is 142 metres thick, S.500 (787427) which is 144 metres thick, and S. 500 (787426) which is 142 metres thick, show a complete succession of the Group (Fig. 2.6).

The lower part of the succession consists of thick dark beds of shale that alternate with thin horizons of shaly limestones. The shale at the lower part of the succession on

the Pendle Hill sections is of a basinal type.

The middle part of the succession on Pendle Hill is mainly shaly limestones dolomitized in some parts alternating with thinner horizons of shale.

The upper part of the succession on Pendle Hill consists of massive layers of limestones, dolomitic limestones and dolostones. Chert layers alternate with those massive limestones and dolostones (Fig. 2.7).

The remaining sections on the Pendle Hill are intermittently exposed. S. 1200 (779415), S. 1300 (770408) and S. 1400 (768400) are mainly shaly limestones resembling the mid-part of the succession. Passing upwards, massive limestones which are silicified and/or dolomitized in some parts are predominant. Chert layers alternate with the limestones and dolostones. In S. 1200 (779415) and S. 1300 (770408) in the upper part of the exposures some horizons of sandy limestones are evident (Fig. 2.7). In S · 1500 (761393) (Fig. 2.6) only the uppermost part of the Pendleside Limestone is exposed and the rocks consist of massive layers of dolostones that are silicified in some parts.

There is a pronounced change in thickness and the spatial distribution of facies of the Pendleside Limestone Group in the Hodder River S. 100 (702339). The thickness of the Pendleside Limestone Group is 157 metres, and the beds are gently dipping northwest with some minor folding. The B. hodderense Beds which mark the base of the Pendleside Limestone Group are well developed and attain a thickness of 5 metres. They consist of hard, grey, extremely fine grained limestones alternating with shale and shaly limestones.

The facies of the lower third of the succession consist of limestones and shaly limestones alternating with thin beds of shale (Fig. 2.7), passing upwards to shaly

limestones and limestones that are dolomitized in some parts and/or silicified in others. The upper third of the succession consists of massive limestones alternating with cherty layers. Some of the massive beds are completely dolomitized and/or silicified. When compared to the Pendle Hill area, the lower part of the River Hodder section is notable for the absence of thick shale beds.

In the Slaidburn area northwest of Clitheroe, four sections of the Pendleside Limestone Group were logged and sampled. The sections are intermittently exposed, and the Pendleside Limestone Group only attains a thickness of 35 metres in this area and is poorly developed. The beds in S.600 (211493) and S.700 (714497) consist of mainly shaly limestones that are partially dolomitized in some parts. In S.800 (715499), limestones that are dolomitized in some parts alternate with the shaly limestones and shales. The limestone beds in the mentioned sections are poorly developed and intermittently exposed (Fig. 2.8). In S.200 (723503), the beds consist mainly of limestone alternating occasionally with shaly limestones and dolomitic limestones. The base of the Pendleside Limestone Group is not exposed in S.200. The base of the Pendleside Limestone Group is marked at the beginning of the Bollandoceras hodderense Beds which are exposed in S.800 (715499) and S.600 (711493). Whereas the top of the Pendleside Limestone Group in the Slaidburn area is marked at the base of the black shales that belong to the lower part of the Bowland Shale Series. At Green Pike S.1600 (576719) is 5 metres thick, and the Pendleside Limestone displays a brecciated and knoll-limestone type lithology which differs remarkably from the Pendleside Limestone exposed at the Pendle Hill sections and the Hodder River section.

In the Holden area near Bolton by Bowland, the Pendleside Limestone Group is exposed intermittently in three sections, each of which complements the other. The

average thickness of the Pendleside Limestone Group here is 96 metres. The B. hodderense

Beds are well exposed in S.900 (765501) and attain their maximum thickness of 9 metres

in this area (Fig. 2.8). The section consists of shaly limestones with thin shales alterna-

ting with limestones that are dolomitized in some parts, particularly in the lower part of

the section. The upper part of the section is mainly massive beds of limestone that are

partially dolomitized.

In sections 1000 (773503) and S.1100 (772494), the B. hodderense Beds are not

exposed and the succession consists mainly of shaly limestones with shales alternating

with limestones that are partially dolomitized. An unexposed part of the succession

occurs in the middle of both sections which obscures a good measure of the Pendleside

Limestone Group in this area. The top of the Pendleside Limestone Group is marked at

the base of the Bowland Shale Group.

In the Salterforth area near Barnoldswick a good succession of the Pendleside

Limestone Group is exposed, section RW + PL (889458) (Fig. 2.6). The lower part of

the succession and the B. hodderense Beds are not exposed. The exposed section is

58 metres thick and the top is marked by a thin (1 metre) shale band overlain by the

Pendleside Sandstone which belongs to the Bowland Shale Group. The facies of the

lower third of this section consists of thick shale beds of basinal type alternating with

thin horizons of shaly limestone. The middle part of the succession is mainly shaly

limestones with shales alternating with limestones that are partially dolomitized. The

upper third of the succession consists mainly of shaly limestones alternating with lime-

stones that are dolomitized and/or silicified in some parts (Fig. 2.7).

In the Lothersdale area, the Pendleside Limestone is poorly exposed (17 metres)

in S.1700 (939445) and 9 metres in S.1800 (943463) (Fig. 2.6). In both sections shaly

limestones are predominent, and some chert bands alternate with the limestones (Fig. 2.7).

2.4 Thickness variation of the Pendleside Limestone Group in relation to structure

In view of the fact that there is a marked difference in the "shelf" and "basinal" facies and their thicknesses, detailed isopachyte and facies analysis has been carried out in order to see if these show any relationship with the tectonic elements in the area.

The Pendleside Limestone Group lies in the Craven Basin in the Central Province. The basin is bounded at its north border by the Askrigg Block and trends east-west, northeast-southwest. It has an irregular shape and an asymmetrical cross-section, George (1958) (Fig. 2.9). The northern margin of the Craven Basin is marked by a series of faults, the North, Mid, and South Craven Faults. The Mid Craven Fault, especially, was active in Dinantian times and may have been the principal axis of subsidence in the Craven Basin (Ramsbottom et al., 1974).

The southern margin of the Craven Basin is more poorly defined and it is largely obscured by post-Dinantian strata. It may be continuous with the Widmerpool Gulf of Derbyshire (George, 1958).

An isopach map of the Pendleside Limestone Group (Fig. 2.10) is constructed on the basis of completely exposed and measured sections. The data was processed using the computer program (Grid) described by Davis (1971). The resultant map shows thickness variation of the Pendleside Limestone Group throughout the area around Clitheroe. The configuration of thickness of the Pendleside Limestone trends northeast-southwest, and generally corresponds to Ramsbottom et al.'s(1974) isopach map of the Pendleside Limestone (Fig. 2.11). Ramsbottom et al.'s (1974) map, although generalized, shows that isopachs in the northern Craven Basin are parallel to the Craven Fault system. This

is in favour of George's (1978) argument which referred to a tectonic origin for the

Dinantian transgressions and regressions rather than a eustatic sea level change.

The detailed isopachyte map of the Pendleside Limestone Group shows a parallelism

with the axis of the Clitheroe Anticline which is one of the principal tectonic folds in

the area (Fig. 2.10). The implication is that the Clitheroe Anticline may have been a

positive feature during Dinantian times which was flanked by more rapidly subsiding areas.

It is worth noting that the Clitheroe reef-knolls (Cycle 2) are also sited along the axis of

the Clitheroe Anticline.

2.5 Textural variation of the facies in different localities of the

Pendleside Limestone Group

A pronounced textural variation of the rocks are observed in different localities

of the Pendleside Limestone Group. In the Salterforth area section (PL+RW) (889458)

(Fig. 2.6), the shales are very fissile and fine grained, and so are the shaly limestones

(Plate 2.1A). The contacts in between the beds are sharp in places and transitional in

others. In general the shaly limestones consist of micrites which in places contain

spicules and calcispheres. With the faunal scarcity (shallow water inhabitants)

this indicates that a quiet water environment prevailed. It is worth noting that

neither oolitic nor peloidal limestone has been found in the Salterforth locality which

contrasts markedly with the beds on Pendle Hill and the Hodder River.

On Pendle Hill, three of the sections of the Pendleside Limestone Group show

a complete succession from the B. hodderense Beds at the base of the group to the shales

of the Bowland Shale Group. These sections S. R8 (788428), S. 400 (787427) and S. 500

(787426) consist of very fine grained shales and very fine grained limestones (sparse biomicrites) (Folk, 1968) in the lower part of the succession (Plate 2.1B). In the middle part, shaly limestones and limestones, in part dolomitized, predominate and many of the limestones have a peloidal or oolitic appearance (sorted biosparites) (Plate 2.1C). These alternate with fine grained micritic sediments, mainly shales. The faunal assemblage is abundant in these peloidal biosparitic limestones and disappears in the finer grained sediments. The upper part of the succession is relatively massive coarse grained limestones, completely dolomitized and/or silicified. The original limestones were probably well-sorted biosparites compared with the lower part of the succession and intercalated shale beds are virtually absent.

In Section S.1200 (779415) only the middle part of the succession is exposed and there are some sandy intervals in the upper parts of the exposure (Fig. 2.7). Texturally, the beds show coarse grained, well-sorted peloidal biosparites indicating a high energy environment. Most of the features in these beds are obscured by dolomitization and/or silicification.

In Section 1300 (770408) the beds show a similarity in texture and composition to those in Section 1200, whilst in Section 1400 (768400), the beds are mainly shaly limestones alternating with limestones and coarse grained peloidal limestones that are dolomitized in some parts. The limestones consist mainly of unsorted biospartites or biomicrite in some horizons. In S.1500 (761393), coarse grained dolostones that are silicified in parts predominate and the exposure is estimated to be the upper part of the Pendleside Limestone Group. The limestone textures are predominantly well-sorted peloidal biosparites.

In the Hodder River section (100) (702399), the beds consist of coarse grained

limestones or dolomitic limestones that are silicified in some parts which alternate with fine grained limestones, shaly limestones and shales. The limestones consist of well-sorted peloidal biosparite or biomicrite, although in some instances micrites predominate. The contacts between the beds are sharp in places and transitional in others. Most of the peloidal limestones are well preserved and not obscured by intense dolomitization and/or silicification as compared with the Pendle Hill sections.

In the Slaidburn area northwest of Clitheroe, four sections are intermittently exposed. Section 200 (723503) (Fig. 2.8) is composed mainly of limestones that are dolomitized in parts and texturally they are coarse grained biomicrites, compared with the rest of the sections to the south of Section 200. Although the remaining sections are poorly and intermittently exposed, namely S.600 (711493), S.700 (714497) and S.800 (715499) (Fig. 2.6), they are fine grained shaly limestones alternating with fissile shale.

In the Holden area, three sections are exposed intermittently and complement each other. Section 900 (765501) is fine grained shaly limestone which consist of micrites at the bottom passing upwards to a relatively coarse grained limestone that are dolomitized in some parts. Sections 1000 (773503) and S.1100 (772494) consist of an alternation of fine grained shaly limestones and coarse grained limestones that are dolomitized in some parts.

2.6 Thickness variation of facies of the Pendleside Limestone Group in relation to the Craven Basin

Data concerning the total thickness of each lithofacies in different localities were processed using the Grid computer program described by Davis (1971). The resultant maps

provided a clear picture of the facies distribution in the basin and outlined the configuration of the distribution of each facies.

The aerial distribution of the total thickness of a lithofacies in a stratigraphic unit is called an isoplith map (Krumbein and Sloss, 1963). The isoplith map of the Carbonates (Fig. 2.12) shows an increase of the thickness of the carbonate facies towards the south-west and a decrease towards the north. Comparing the carbonate isopliths with the general configuration of the basin which trends northeast-southwest in direction the increase of the carbonate is towards the presumed shelf areas of the basin. Accordingly in the centre of the basin the carbonates show a remarkable decrease in thickness.

The shale isopliths (Fig. 2.13) show a pattern which is the reverse of that of the carbonate. The shale isopliths decrease towards the shelf areas of the basin and show an increase towards the basinal parts of the area. This is clearly indicated in Fig. 2.13, where the shale is at a maximum thickness in the mid-part of the map.

The shaly limestone isopliths (Fig. 2.14) resemble the carbonates in configuration and outline the boundary between the carbonate and shale facies.

Further analysis was carried out as to calculate the percentage of each of the three facies in the Pendleside Limestone Group. The carbonate percentage (Fig. 2.15) shows a distinct increase towards the northern edge of the map. The northern edge of the map corresponds to the wedging-out of the basin towards the Askrigg Block. The increment is very steep and resembles the steep slope of the Askrigg Block towards the basin. The percent carbonate decreases in the middle of the map whereas the shale percent increases in the same direction (Fig. 2.16). The superimposition of Figs. 2.15 and 2.16 suggests that the shale was deposited in the basinal areas whereas the carbonates are deposited on the shelf areas.

The shaly limestone percentage (Fig. 2.17) lines the boundary between the carbonate increment and the shale, although it shows some increment towards the carbonate.

A lithofacies map (Fig. 2.18) shows the aerial distribution of limestone-shale in the studied area. The limestone areas consist of 50% or more limestones and/or dolostones, whereas the shale area consists of 50% or more shale. The pattern of the distribution indicates that the limestones are well developed on the shelf areas and were probably deposited in a relatively shallow water, high energy environment. The shales which occupy the central part of the area were, on the other hand, probably deposited in deeper-water, low-energy environments away from the basin margin. The intermediate position of the shaly limestones suggests that the lateral transition from limestone to shale was gradational.

2.7 Age, and faunal distribution of the Pendleside Limestone Group

Most of the fossils found in the Pendleside Limestone Group are benthic foraminifera coexisting together with bryozoans, echinoderms, crinoids, algae, algal products (calcispheres) and scarce corals. All the benthic foraminifera of the Lower Carboniferous are mostly shallow water inhabitants (Mamet & Skipp, 1972), and the faunal assemblage in the Pendleside Limestone Group indicate a late Asbian age (Turner et al., 1979). The foraminifera found in the Pendleside Limestone never favoured deep water environments such as basinal shales, so their occurrence suggest the prevalence of shallow water environment.

The following genera of foraminifera have been found in the Pendleside Limestone: Endothyranopsis sp. (plates 2.2A and B), Plectogyra sp. (plate 2.2C), Archaediscus sp.

(plate 2.3A), Brunsiella sp. (plates 2.7A and B), Diplosphaerina sp., Eotubertina sp. (plates 2.6A and B), Draffania sp. (plate 2.5A), Earlandia sp. (plate 2.6C) and Tetraxis sp. (plate 2.7C). All indentifications are according to Hallet (1967). Other fragmentary fossils also imply shallow water deposition. These include: bryozoans (plates 2.3C and 2.4A) which occur with the above mentioned foraminiferal assemblages, and echinoderm plates (sometimes syntaxially overgrown) (plate 2.3B). Perhaps the most abundant fossils in the limestones of the Pendleside Limestone are calcispheres, some of which contain radially deposited calcite (plates 2.5B and C).

Conodont biostratigraphic studies by Metcalfe (1976) have enabled the correlation of the six cycles of Ramsbottom (1973) throughout the Craven Basin. He correlated the Draughton Limestone with the Pendleside Limestone Group in the Rad Brook section (RB) (788428) on the Pendle Hill (Fig. 2.19). His correlation was based mainly on the conodont Gnathodus girtyi and the other conodonts such as Gnathodus bilineatus which are found in the Draughton Limestone in Embsay Beck.

The results confirm the attenuation of the Dinantian succession in the Skipton Anticline area. Also the shallow water fossil assembleges suggest that the Craven Basin was a continuously subsiding shallow water basin.

2.8   Conclusions and remarks regarding the sedimentation of the
        Pendleside Limestone Group

The Pendleside Limestone Group was deposited in the Craven Basin after the beginning of the Asbian stage of the Dinantian. The basin was a trough-like depression, asymmetrical in cross-section and trended northeast-southwest. The northern edge of the basin is bounded by the southern edge of the Askrigg Block and slopes steeply to the south

and southeast towards the centre of the basin, whereas the southern edge of the basin slopes gently northwards towards the centre of the basin.

The period of deposition began a little while after the beginning of the Asbian stage as this was confirmed by the microfaunal (foraminifera and conodonts) assemblege identified throughout the succession. Differential subsidence with consequent facies variations were a feature of the sedimentation of the Pendleside Limestone Group. The influence of tectonics on the facies distribution is implied by the pronounced facies changes of the Pendleside Limestone which take place between the different anticlinial blocks.

These results are of some significance concerning the controlling mechanism of transgressions and regressions and facies changes in the Dinantian. This brings us to the two schools of thought regarding the controlling factor of sedimentation of the Dinantian:-

i) Ramsbottom (1973) divided the Carboniferous into six major cycles. Four of these cycles are attributed to major transgressions and regressions due to eustatic change in sea level. The remaining two cycles are subdivided into groups of minor cycles.

ii) George (1978) assigned a tectonic origin for Ramsbottom's six major cycles and he provided evidence favouring a tectonic origin; he also provided evidence against the eustatic change of the sea level that was proposed by Ramsbottom (1973).

The evidence against the eustatic sea-level change includes:

1) The confusion of the cycles proposed by Ramsbottom (1973). The faunal assemblege at the end of some of the cycles do not coincide with some beds· that fall within the same cycle, but belong to the successive cycle.

2) Differences in magnitude of Dinantian cycles are subjectively conceived, and were not measured by eustatic change of sea-level fluctuation or

intensity of erosion during regression or by extent of overstep during

transgression.

3)   Facies and the depth of sedimentation. Ramsbottom (1973) over-

generalized the rock types, and the transgressions and regressions, which

George (1978) found to be misleading, especially if the rock was not in

its stratigraphical and structural context of sequence and range.

4)   The rhythms and microfossils do not coincide and correlate in range

throughout the cycles in different localities.

5)   The major cycles and stages have different boundaries.

6)   There is a relationship between the depth of the basin and the thickness

of sediments which the writer finds to provide a good evidence in favour

of George (1978). The Dinantian was mostly deposited in shallow if not

very shallow water in reference to sea-level. This is also supported by

the shallow water faunal assemblage found. The thickness of the sediments

(1000 m - 2500 m) and the occurrence of shallow water fauna implies a

shallow subsiding basin. The arguments put forward by George (1978)

against Ramsbottom's eustatic model find some support in the present study.

The Pendleside Limestone Group also implies a tectonic origin for a

subsiding sea floor. Some evidence regarding the subsidence of the sea

floor:

a)   The faunal assemblage (microfossils) and textural characteristics

imply a shallow water environment of sedimentation of the

Pendleside Limestone Group. In order to account for such a

thickness of shallow water sediments, a subsiding sea floor during

sedimentation must be invoked.

b) The spatial distribution of the thickness of the Pendleside Limestone Group and its parallelism to major tectonic elements such as the trend of the Clitheroe Anticline can not be coincidental. It suggests a fundamental relation between sedimentation and the tectonism in the Craven Basin.

c) The sharp contacts between the shales and limestones could not have been brought about, if the change in sea level was eustatic. Because if the change in sea level was eustatic, transitional contacts in between the beds would be observed vertically and laterally.

d) The differential type of deposition over short distances. The Pendleside Limestone Group shows a pronounced facies change in different localities over very short distances.

The foregoing observations lead to conclude that the Pendleside Limestone was deposited in a shallow water basin which was continuously subsiding. The subsidence reflected variation in lithological facies, sedimentary features, e.g. sharp contacts between bedding planes, and the thickness of sediments.

Chapter Three

SEDIMENTATION

Chapter Three

SEDIMENTATION

3.1   Introduction

The Dinantian sediments of the Craven Basin are folded into a series of NE-SW

trending anticlines and synclines known as the Ribblesdale Fold Belt. The Craven Basin

forms part of the block-basin structure of the north of England (Bott and Johnson, 1967).

This basin is separated from the Askrigg Block to the north by the Craven Fault System

which consists of three princip   faults, the North, Mid and South Craven Faults.

Sedimentation in the Craven Basin began in late Courceyan times and continued

without a major break throughout the Dinantian. In the Skipton area approximately 1000

metres of interbedded limestones and shales with occasional subordinate sandstones

accumulated, whilst in the Clitheroe area to the south, the succession reaches approxi-

mately 2000 metres (Turner et al., 1979). All the Major Cycles of Ramsbottom (1973) are

recognizable throughout the area as discussed in the previous chapter.

3.2   Facies variation of the Pendleside Limestone Group throughout

        the Ribblesdale Fold Belt

The Pendleside Limestone Group in the Clitheroe area and the Draughton Limestone

in the Skipton area belong to the Fifth Group of Minor Cycles (Asbian Stage). In the

Skipton area the upper part of the Asbian Stage is represented by the Draughton Limestone.

This consists of 30 metres of thin graded beds of coarse bioclastic limestone associated

with intraformational limestone conglomerate (Turner et al., 1979). These coarse grained

limestones pass up rapidly into thin calcite mudstones with horizontal laminations which

are, in places, extensively bioturbulated (Fig. 3.1A). The Draughton Limestone

including Tiddeman's Breccia is interpreted as a proximal turbidite deposit (Ramsbottom

et al., 1974). It is derived partly from the reef belt of the same age which developed

along the northern margin of the Craven Basin (Fig. 3.2).

The lateral equivalent of the Draughton Limestone in the Clitheroe area is the

Pendleside Limestone Group (Metcalfe, 1975; Turner et al., 1979) and this has an

average thickness of 90 metres. It consists of fine-grained to coarse-grained bioclastic

limestones with shales which have suffered extensive dolomitization and chertification.

The Pendleside Limestone Group is believed to represent a more distal turbidite sequence

than the Draughton Limestone. This is certainly the case in the central part of the

Clitheroe Anticline, but in other areas, e.g. the Salterforth area, the Pendleside

Limestone shows considerable variation (Fig. 3.1B, C and D).

In the Salterforth area the Pendleside Limestone Group consists of fine-grained

shaly argillaceous limestone alternating with thick beds of shale. The limestones have

nodular or blocky habit of jointing in some horizons (Plate 3.2A) and are rich in spicules

and calcispheres. The contacts in between the shaly limestones and shales are transitional

in places (Plate 3.1A and B) with occasional sharp contacts (Plate 3.1C). The base of

the Pendleside Limestone Group is not exposed in the Salterforth area section (PL+RW)

and the exposures are considered by their appearance to be a non-turbiditic sequence

compared with other localities, e.g. Rad Brook or Slaidburn area. The Salterforth section

is considered to be an inter-fan deposit due to the absence of coarse-grained detritals

and predomin nce of fine-grained deposits. Such fine-grained material can be deposited

from continuous hemipelagic fall-out and also during the winnowing stages of particles.

This may occur from a stationary turbid cloud left after the passage of a turbidity current

(Hesse, 1975; Mutti, 1977; Krause and Oldershaw, 1979).

In the Pendle Hill area and in the Rad Brook section the sequence can be divided into three parts. The lower part of the Pendleside Limestone succession on Pendle Hill consists of thick beds of shale of basinal type (Fig. 3.1C, Plate 3.2B). The middle part consists of shaly limestone alternating with thin cherty limestone beds (Plate 3.2C and 3.3A). The beds are highly weathered and very fissile. The upper part of the Pendleside Limestone Group consists of massive bedded limestones and dolostones with occasional very thin horizons of shale. The limestones are thinly laminated and in some places graded bedding is observed (Plate 3.7A and B). Occasional chert nodules also occur in the limestone body (Plate 3.3B). Dolomitization of the limestones is a prominent feature in the upper two thirds of the succession. The contacts between the beds are sharp in most of the succession, especially at the base of beds (Plates 3.3C and 3.4A and B) but in some places the contact appears to be transitional (Plate 3.4C).

Petrographic examination of samples collected from Pendle Hill sections reveal that the limestones show an increasingly coarse texture upwards (Plate 2.1C). This suggests a general shallowing in the environment of deposition and proximity to surface conditions.

To the north of the Slaidburn area the Pendleside Limestone succession is much thinner and consists of limestones and submarine limestone breccias separated by a non-sequence (Parkinson, 1936) (Fig. 3.1D). Occasionally reef knolls are found in the chertified limestones and dolomitization is observed. The beds consist of coarse-grained fossiliferous limestones with crinoid stems and echinoderm plates.

In the Hodder River section (100) the Pendleside Limestone Group shows its maximum thickness of 190 metres. The lower part of the succession consists mainly of alternations of thin beds of shale (30 - 40 cm) in thickness and shaly limestones (40 cm) in thickness, the contacts generally being transitional (Plate 3.5A and B). Passing up the

succession the shale beds diminish and grade into shaly limestone (Plate 3.5C). Towards the top part of the succession these shale beds thin out and massive limestone beds (1 - 3 metres) with chert bands (10 cm) and sharp contacts become a prominent feature (Plate 3.6A, B and C). Petrographic examination of thin section of the samples collected revealed ten alternations of fine-grained micritic limestones scarcely fossiliferous and coarse-grained peloidal or skeletal limestones fossiliferous in some parts (Plates 2.2A and 2.6C respectively). This alternation is thought to correspond to periods of maximum and minimum shale or peloidal limestone formation in contrast to their interpretation as transgressions and regressions by Ramsbottom (1973).

In all, the field evidence and petrographic examination of the Pendleside Limestone Group revealed that these limestones are predominantly distal turbidities deposited above the carbonate compensation depth in a shallow water basin. The following evidence is considered critical:-

1) The deposits were influenced by periods of maximum and minimum shale or peloidal limestone formation as can be indicated by the alternation of fine-grained limestones and coarse-grained peloidal limestones throughout the Pendleside Limestone Group.

2) The contacts in between shale beds and limestones being sharp at base and transitional at top.

3) Facies variation of the Pendleside Limestone Group throughout the study area (Fig. 3.1A, B, C and D).

4) Graded bedding found in some localities (Plate 3.7A and B) indicate a turbiditic origin for the Pendleside Limestone Group.

3.3   Turbidity currents and their application to the Pendleside Limestone Group

For many years the study of turbidite sequences has focussed on coarse-grained (sand size and coarser) deposits. The finer rocks alternating with the coarser turbidities have been neglected and have only recently attracted some attention. The occurrence of both turbiditic and non-turbiditic layers among these fine-grained rocks is now generally acknowledged (Scholle, 1971; Hesse, 1975; Mutti, 1977; Krause and Oldershaw, 1979). However, transport and deposition of both types of fine-grained and coarse-grained deposits raises a number of unsolved problems. The biggest problem is still, in many cases, the distinction between the turbiditic and the non-turbiditic sediments, as shown by the degree of uncertainty expressed with respect to this question in many published papers. In Boumas (1962; 1972) structural scheme for turbidities, no criteria were given for the distinction of distal turbidities, e.g. fine-grained limestones deposited from the tail of a turbidity current, although these have subsequently been developed by Hesse, (1975).

In the Pendleside Limestone Group, however, deposition of fine-grained sediments from turbidity currents obviously took place on a sloping sea-bottom by analogy with recent turbiditic sediments. However, recent turbiditic sediments show that not all the fine-grained sediments carried by turbidity currents are flushed out from the areas of sloping sea-bottoms into basins with horizontal bottoms.

The problem envisaged in this situation is that the density and thickness (hydraulic depth) of the currents required for deposition of a fine-grained sediment of appreciable thickness would appear to be relatively high. The resulting driving force would not allow the current to decelerate sufficiently on a sloping sea-floor and would prevent the fine-grained suspended sediment load from being dropped. Very little is known on the deposition of fine-grained sediments from suspension. Nevertheless, Hesse (1975)

provided a good explanation regarding the deposition of fine-grained sediments from cloudy suspensions. He stated that the deposition of fine-grained, cohesive material is fundamentally different from that of coarser, cohesionless materials. Electrostatic forces act between the fine-grained particles which at the salinity of sea water have a net attractive effect. The collision of particles leads to flocculation. The rate of flocculation depends on particle concentration and therefore on capacity. Capacity for fine-grained suspended sediments is independent of flow conditions and is practically unlimited except by the viscosity of the flow. The transport rate of fine-grained material therefore depends on the availability of such material rather than on the flow characteristics. Other factors such as density difference of the shallower warmer (and probably less saline) water entrained in the turbidity current and the cooler ambient sea water at greater depths where deposition from the turbidity current may eventually occur. The density difference can then be employed to carry suspended sediments without producing a driving force on the turbidity current flowing on a sloping sea-floor; and the temperature effect will thus increase the capability of a turbidity current to deposit fine-grained material on sea-floor. Deposition is due to flocculation and addition to the fine-grained sediments surface. The thickness of the deposit is controlled, among other factors, by the concentration and the length (duration of passage) of the flow. At a later phase the current may have slowed down substantially but still carry significant amounts of fine-grained material due to the temperature effect. Deposition would now be controlled predominantly by the settling velocity of the fine-grained particles.

If the factors mentioned (temperature difference between turbidity current and ambient cooler water in relatively greater depths, density difference) are correct, then the deposition of large amounts of fine-grained material by turbidity currents on sea-floor no longer poses a problem.

3.4 Environment of deposition of the Pendleside Limestone Group

The deposition of the Pendleside and Draughton Limestones are thought to be as a result of passage of turbidity current originated from a northerly source as indicated by their lithologies. The two limestone groups (Pendleside and Draughton) are classified in terms of distance, the Draughton Limestone being the proximal deposit of the turbidite whereas the Pendleside Limestone is distal equivalent (Fig. 3.5).

The following interpretation of the environment of deposition of the Pendleside Limestone Group is based mainly on field observation, thin section examination of samples collected from different localities and the spatial distribution of the sediments in regard to the basin of deposition and its relationship to wave activity and proximity to the wave-base. With regard to these factors the environment of deposition of the Pendleside Limestone Group can be divided into two distinct parts:-

A) Sediments deposited above the wave base prior to subsidence. This kind of sediment is distinguished by coarse-grained clasts, examples of which are the massive peloidal limestone beds in the upper two thirds of the succession on Pendle Hill, Hodder River section, Lothersdale sections, and the sections in the Slaidburn area. Although these horizons represent maximum critical thickness of sediments prior to subsidence (regressive phases of the sea-level according to Ramsbottom, 1973), they also indicate a high energy environment in which the sediments are reworked and deposited above the wave-base. They are influenced by wave action and biogenic activity as indicated by the abundance of fossils preserved in these limestones. From the overall picture constructed· from the above evidence and by analogy with present day sedimentation in carbonate accumulating seas, it is suggested that the deposition of sediments in shallow water environment was subject to and influenced by wave activity prevailing at the time of

deposition of the sediments. It is worth mentioning here that diagenesis, i.e. dolomiti-zation and silicification, have obscured most of the original fabrics and pre-diagenetic features of the Pendleside Limestone Group and created new fabrics and new features which will be the subject of discussion in the next chapter.

B) Sediments deposited below wave-base after subsidence. To this category of sediments belongs the lower third succession of beds on Pendle Hill and some of the fine-grained limestones, shaly limestones and shales that alternate with the peloidal limestone horizons higher up the succession of the Pendleside Limestone Group. In the Hodder River section, the lower third of the succession, which consists of thick beds of shale alternating with shaly limestones, is also placed in this category as well as some fine grained shaly limestone beds higher up the succession. In the Salterforth area the whole succession belongs to this category of sediments. They consist of alternations of thick beds of shale (2 - 3 metres) and shaly limestones (3 - 4 metres) in thickness. Petrographic examination of thin sections of samples collected from the mentioned localities reveal that the shaly limestones consist of fine-grained (micritic) limestones with scarcity of faunal assemblage except for a few transported fragments of shell debris. This suggests that these sediments were deposited in a relatively deeper water environment.

All these horizons represent post-subsidence depositional phases of the sea-floor which correspond to the transgressive phases of Ramsbottom (1973); they also indicate sedimentation in a quiet water environment, typical of deposits below the wave-base. This is indicated by the predominence of fine-grained limestones, shaly limestones and shales of basinal types. A confirming indication of a relatively deeper water environment is the absence of a faunal assemblage.

3.5   The controlling mechanism of sedimentation of the

Pendleside Limestone Group

Sedimentary cycles are of widespread occurrence and are known from many parts of the geological column. Simple cycles such as banded and varved deposits, may be controlled by seasonal variations, but cycles of sedimentation which involve a repetition of strata laid down under differing environmental conditions require a more complicated control mechanism.

There are two schools of thought regarding the mechanism responsible for the Carboniferous cyclic sedimentation of which the Pendleside Limestone Group provides a typical example. The first theory is that of eustatic changes in sea level. The eustatic sea-level change is supposed to have influenced sedimentation and deposited the sediments rhythmically in the Carboniferous sea. This is favoured by Ramsbottom et al. (1974).

Eustatic changes in sea-level may be either transgressive with rising levels of sea and shoreline or regressive when these levels fall. The changes must equally affect the centre and the margin of basins. Normally the thickness of sediments laid down at the margins would be equal to the amount of eustatic rise, but this is not found in Carboniferous basins. To explain the extreme thinning of sedimentary cycles at the margin of Carboniferous basins the eustatic changes need to be reversible, namely a rapid rise in sea-level followed by a return to, or nearly to, the original level.

Eustatic changes of sea-level may be caused by the following processes:

A) Changing the total volume of the oceans. The only known process which can cause rapid sea-level fluctuations by volume changes in the oceans is glacial control. It has been suggested to explain Carboniferous cyclothems by Wanless and Shephard

(1936); Wheeler and Murray (1957); and Ramsbottom et al. (1974).

B) Changes in the topography of the ocean floor. These changes take place by subsidence of trenches and basins; by the infilling of these with sediments; by delta formation; by decrease in the area of continents; by mountain building; and by the formation and decay of oceanic ridges and rises (Bott and Johnson, 1967). Basin formation and infilling has been suggested as a mechanism in the formation of sedimentary cycles by Wells (1960), but it can only cause small sea-level changes.

Therefore, the glacial control appears to provide the most realistic eustatic mechanism for cyclic sedimentation. Some of the evidence might be true regarding the deposition of some of the major cycles, but application of eustatic sea-level changes to explain minor transgressions and regressions is more difficult as this will be discussed later in this chapter.

The second theory favours the influence of tectonic activity upon the sedimentation of the Six Major Cycles of the Carboniferous strata. This is favoured by Bott and Johnson (1967) and George (1978). Regarding the cyclic sedimentation of strata, Bott and Johnson (1967) presented these relevant criteria to test and compare whether the sedimentary sequence is of a eustatic or tectonic origin.

The significant test concerns the variation in the deposits of a sedimentary cycle between the centre of a subsidiary basin and the marginal regions where subsidence is much less (Fig. 3.3). Maximum subsidence takes place in the centre of the basin, and it becomes progressively reduced to zero towards the margins. This fits very well to the thickness variation of the Pendleside Limestone Group, where the thickness is at a maximum in the mid-basin and diminishes to almost zero at the margins. Ramsbottom et al. (1974) presented an isopach map (Fig. 2.11) of the Pendleside Limestone Group, the northern

margin of which is zero or absent.

Eustatic rise in sea-level must equally affect the margins and the central part of deposition. The margin will suffer negligible subsidence compared to the central region. For the eustatic hypothesis this means that deposition near the margin of the basin should take place earlier in the cycle, after the eustatic rise in sea-level, and erosion should occur later in the cycle as sea-level returns to the initial value. At the margin, therefore, remnants of sediments characteristic of the early part of the cycle should be present and there should be evidence of strong erosion between cycles(Fig. 3.3A). In the Pendleside Limestone Group there are no unconformities developed between the minor cycles, but there is a major unconformity at the top of the Pendleside Limestone Group, the trace of which is found at the top of the Draughton Limestone, the lateral equivalent of the Pendleside Limestone Group. Also, there is a well-developed unconformity at the top of the Pendleside Limestone in the Slaidburn area. On the other hand, the tectonic hypothesis suggests that marginal deposits should consist mainly of sediments characteristic of the top of the cycle and that strong local erosion should be lacking (Fig. 3.3B).

According to the tectonic hypothesis local crustal subsidence causes fluctuation in the sediments being deposited in the shallow sea so formed. Before presenting the mechanism responsible for the Pendleside Limestone cyclic sedimentation the following observations are relevant:

1) The Pendleside Limestone succession consists of alternation of shale beds, shaly limestones and limestones or dolostones. The shales represent facies of basinal type, whereas the limestones represent facies of shallow water environment. This is indicated by the occurrence of inhabitants that favour living in a shallow water environment. Besides the occurrence of peloidal limestones throughout different horizons indicate a high energy environment which is typical above wave-base level. The shales are devoid of

faunal assemblege and consist of fine-grained micritic material.

2) The thickness of the Pendleside Limestone Group averaging 90 metres compared with the shallow depth of the basin as indicated by the faunal assemblage present suggest a subsidence in the plane of deposition.

3) The Mid-Craven Fault that borders the Craven Basin from the north and trends in an east-west direction was active at the Dinantian times (Ramsbottom et al., 1974).

4) The absence of unconformities in the Pendleside Limestone Group rules out the eustatic sea-level change mechanism (Bott and Johnson, 1967).

5) As a supplement to the preceeding observation, no remnants of sediments characteristic of the early part of the cycle are present throughout the margin of deposition in the Pendleside Limestone Group.

Therefore, the following mechanism is proposed for the Pendleside Limestone cyclic sedimentation:-

As the turbidity currents flowed they continuously deposited sediments in the Craven Basin from its northerly source. Evidence indicates that the Mid-Craven Fault was active in the Dinantian times (Ramsbottom et al., 1974). This created downward wedging of the basin. Now the continuous flow of the turbidity current and the accumulation of sediments on sea-floor was controlled by the Mid-Craven Fault rhythmic subsidence as sediments attained a certain critical maximum thickness prior to subsidence. But the wave-action as the sediments were infilling the basin reworked the sediments and produced the coarse-grained high energy deposits, e.g. peloidal limestones that are found alternating with fine-grained sediments throughout the Pendleside Limestone Group. This means that the peloidal limestones represent the maximum critical thickness prior to subsidence, after

which subsidence of the sea-floor must have happened. The subsidence lowered the plane of deposition below the wave-base to a more quiet environment typical for the deposition of shale (Fig. 3.4). This mechanism accounts for the alternation of the shale beds with the peloid limestones throughout the Pendleside Limestone Group.

3.6   Discussion and conclusions

The Pendleside Limestone Group was deposited in a shallow water as indicated by the faunal assemblege and the presence of the coarse-grained peloidal limestone beds that indicate high energy environment of deposition. The basin of deposition suffered many episodes of subsidence due to the activity of the Mid-Craven Fault as shown; this resulted in the accumulation of thick sequence of sediments in a shallow basin that can be accounted for by the subsidence of the basin floor.

The origin of the sediments composing the sequence of the Pendleside Limestone Group is thought to be from the turbidity currents originated from a northerly source as indicated by the presence of reef-knolls (located in the north) of Asbian age (Cracoe reef-belt). The reef-knolls are also present in the Pendleside Limestone sequence in the Slaidburn area where they are associated with proximal turbidites. In other localities the Pendleside Limestone sequence is considered to represent distal turbidites.

Eustatic changes in sea-level can allow the formation of cycles of sedimentation but the apparent absence of a mechanism for repeated eustatic movements of the right type, together with the absence of marginal deposits and unconformities which they would be expected to produce, precludes the application of this hypothesis to explain the thick Pendleside Limestone cyclic sequence.

The alternative explanation of repeated differential vertical movements of the sea-floor is considered to be more probable.

PART II

DIAGENESIS

Chapter Four

CARBONATE DIAGENESIS AND CEMENTATION

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4.2   Carbonate diagenesis in the Pendleside Limestone Group

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Chapter Four

CARBONATE DIAGENESIS AND CEMENTATION

4.1   Introduction

The concept of diagenesis deals with the changes that take place in sediments from immediately after deposition up to final lithification.

Lithification and diagenesis of carbonates can take place in a variety of environments (Folk and Land, 1975) including deep marine environments (Fisher and Garrison, 1967); shallow marine environments (Hanshaw et al., 1971; Badiozamani, 1973; Dunham and Olson, 1978); subaerial environments (Friedman, 1964); and in the deeper subsurface (Friedman, 1968). These are all preserved in the fabrics of the indurated carbonate rocks, which are the product of various diagenetic processes that these carbonate rocks had undergone in their environments.

The primary pore spaces (50% - 70%) and the secondary pore spaces produced by fossil leaching, fracturing, have been almost completely reduced through the various diagenetic processes which altered the rocks of the Pendleside Limestone Group.

These diagenetic changes not only resulted in pore volume reduction, but also in mineralogical change, e.g. calcite to dolomite; additions and removal of material, e.g. dissolution of calcite to provide CO_3^{-2} ions necessary for dolomite growth; textural and probably structural modifications. These changes are indicated in the limestone fabrics by the occurrence of cementation, neomorphism, replacement, compaction, leaching and cavity infilling.

Most of the early diagenetic processes and/or changes which took place while the sediments were still in contact with sea water could be completely changed, or obscured by the subsequent changes following burial or subaerial exposure to the surface.

Most of the processes that act on carbonate rocks during diagenesis accomplish one or more of the three following operations:-

i) Cementation:- Cementation is generally considered to be the growth of new crystals into void spaces, whatever the origin of the void space. The new crystals occupy spaces that formerly were occupied by fluid, commonly water or air plus water, where the cementation took place within the vadose zone. The pore space may be primary, for example cavities that are a result of depositional processes. They may occur between carbonate grains, within fossil shells, or within the cavities created by organisms such as corals when they build a partially open framework. In addition much cementation takes place within secondary pore space that is produced by dissolution or fracturing of carbonate grains and cements.

The mineralogy of the carbonate cements naturally depends on the composition of the fluid from which the crystals grow. In general, when the cementing crystals grow from sea water or a similar solution, the minerals aragonite and high magnesian calcite normally form, but due to the metastability of both minerals, they alter to the more stable phase of low magnesian calcite in form of micrite or sparite (Folk and Land, 1975).

ii) Dissolution:- which produces void spaces within the rock by removal in solution of previously existing carbonate minerals. In most natural waters high magnesian calcite and aragonite will be more soluble and metastable than low-magnesian calcite. Shallow sea water generally is saturated with respect to both aragonite and calcite. Given sufficient time, all the metastable calcium carbonate minerals will be dissolved and/

or replaced by low magnesian calcite.

Ancient carbonate rocks commonly contain abundant voids. Many of these may be produced by simple dissolution of limestone that makes void spaces of all sizes. The dissolution may be selective, for example, only the aragonitic part of a mollusc may be removed; or non-selective where water moves along joints and enlarges the joints and locally produces enlarged cavities that will be filled later on. In all cases of dissolution, it is presumed that the pore water is not the normal sea water at the time of the dissolution but was undersaturated with respect to the mineral removed. In addition it can also be assumed, because of the relatively low solubility of calcium carbonate in most natural waters, that a very large number of pore volumes of fluid passed through the rock and caused the pore spaces. In carbonates, the dissolution can only be accompanied by a large volume of moving water through the pore spaces.

iii) Replacement:- which involves the essentially simultaneous dissolution of existing minerals and the precipitation of a new mineral. In most ancient carbonates the primary carbonate rock particles such as ooliths, and metastable cements such as aragonite, are represented in the rocks by a different mineralogy or different crystal size. This is obvious from the recognition of ghosts of the primary material, represented by inclusions, pseudomorphs, or reproduction of an original outline. It is obvious, in most of these, that the original material could not have simply been dissolved away, and the new phase precipitated as cement. In order to preserve the evidence of the original material, the growth of the new mineral must have taken place essentially simultaneously with step-by-step dissolution of the earlier material. This implies that the water must be in a delicate balance so that it will dissolve one phase and precipitate another at the same time.

4.2   Carbonate diagenesis in the Pendleside Limestone Group

4.2.1   Methodology

Fieldwork included logging and sampling of the exposures in 19 localities. The logging included detailed field description of the lithology, structure, and facies variation of the Pendleside Limestone Group at every locality.

Generally, the sampling of the exposures is at intervals of one metre or less. Deviation from this scheme of sampling was necessary when thin horizons of lithologically variable facies were encountered. A thin section was made of each sample and stained with potassium ferricyanide plus alizarin Red S in order to distinguish the calcite (pink coloured); ferroancalcite (mauve-blue coloured); dolomite (colourless); and ferroan dolomite (turquoise coloured), (Evamy, 1963; Evamy and Shearman, 1964; Dickson , 1965) (Appendix A).

The staining proved to be very effective in distinguishing calcite, ferroan calcite, dolomite and ferroan dolomite which are all present in the Pendleside Limestone Group. Compositional zonation in carbonate cement crystals was also effectively revealed.

4.2.2   Diagenetic fabrics in the Pendleside Limestone Group

Bathurst (1958) gave an account on some of the diagenetic fabrics in the British Dinantian limestones. His work was mainly based on the fabrics found in samples collected from the Avon Gorge, North Wales, the Askrigg Block, and the reef knolls in the Clitheroe area. He discussed mainly the textures and structures he found in thin section examination.

The diagenetic processes had a great influence on the fabrics of the Pendleside

Limestone Group and resulted in substantial alteration of the original sediment. Most of the original fabrics at the time of deposition are altered and obscured by diagenesis; new fabrics were created which will be discussed later in this chapter.

There are two kinds of carbonate cementation in the Pendleside Limestone Group:-

1) Non-ferroan calcite cement:- which precipitated from sea water or by algal secretion. This can be seen in the syntaxial overgrowths of some echinoderm plates.

2) Ferroan-calcite cement:- which comprises almost all the cement in the Pendleside Limestone Group. The process of precipitation and re-distribution of the ferroan calcite involves large volumes of per-colating solutions and open pore spaces for the circulation to take place.

It is more likely that the precipitation of ferroan calcite as a second generation cement took place before compaction and in a shallow water, e.g. vadose zone, before deep burial, where circulation of fluids was more likely.

Some of the syntaxial overgrowths in echinoderms have ferroan calcite cement at their fringes immediately after the iron-free calcite cement which is considered to be a first generation cement. This suggests that the precipitation of the second generation cement (ferroan calcite) was continuous after the first generation iron-free cement (Plate 4.6B). Perhaps compaction brought the second generation cement to an end. This is postulated by the reduction of pore space and restriction of the circulating pore fluids by compaction. After all, cementation itself is a pore destroying process because it involves the blocking of the pore cavity by cement. After compaction, only the development of pressure-solution on local scale, e.g. grain to grain or pressure-solution on a large scale, e.g. stylolites, took place.

The diagenetic processes and the resultant fabrics involves the following:-

i) Alteration of framework constituents:- The main allochemical components of the limestones in the Pendleside Limestone Group are foraminiferal tests, broken shells of molluscs, ooids, peloids, calcispheres and spicules (Fig. 4.1A) (Plates 4.3C, 4.4A, B and C).

Many of the sand-sized components show the development of micrite envelopes (Bathurst, 1966). These are formed by the centripetal replacement of grains by micrite. The process involves the activity of boring algae which bore into the surface of carbonate particles. After death and decay of the algal tissue the bored tubes are vacated and become filled with micrite. The role of algae suggests that the process takes place in a shallow water environment where circulation of fluids is possible.

Kendal et al. (1966) suggested that the survival of the micritic material in ancient limestones is due to its content of organic material, which has a high mechanical strength. They further suggest that moulds were preserved during diagenesis because of the presence of organic material which is more resistant to dissolution than metastable carbonate minerals.

Winland (1968) discovered that some recent micrite envelopes are high magnesian calcites, and he suggested that the stability of the micrite envelope follows from its mineralogy. The high magnesian calcite would not dissolve but would simply lose its Mg^{+2} to be replaced by low magnesian calcite. Bathurst (1975) sympathized with this view particularly when he found some collapsed micrite envelopes which were broken during compaction. He thought that these were brittle at the time of fracture and not simply elastic organic matter. He suggested that recent micrite envelopes which are aragonitic would not be transformed to calcite in the diagenetic environment without first being dissolved. Such aragonitic micrite envelopes could be stabilized by being transformed to

high magnesian calcite which subsequently loses it's Mg^{+2} and stabilizes into low magnesian calcite.

ii) <u>Granular cementation:</u>- Generally the cementing material is clear crystalline calcite which was evolved in one of two ways. In places it appears to be either as a pore cement or a drusy mosaic chemically deposited from solution onto the free surfaces of framework constituents (Bathurst, 1958).

The granular cementation process consists of the chemical deposition of material from solution onto a free surface (Fig. 4.2). It involves the growth and expansion of one grain on the account of it's neighbours (Fig. 4.1C and D). Examples in the Pendleside Limestone Group of cement growth in the pore spaces are shown in Plate 4.5A, B and C.

The drusy mosaic cement is formed in the chambers of fossils where the grains are small near the wall and increases in size away from the wall (Fig. 4.3) (Plate 4.5C). As a matter of fact, the distinction between granular cementation and drusy growth is according to their site of deposition; the granular cement grows between detrital particles whilst drusy mosaic grows into all other cavities, for example in fossil chambers.

Sometimes the host or the main framework of the limestone are single crystals (e.g. crinoid fragment) and the cement forms a single rim in a lattice continuity with the single crystal; the cement is called a rim cement (Bathurst, 1958).

A mosaic grain can grow if the deposition of material is in lattice continuity with, or syntaxially with a free crystal face (Goldman, 1957). In this case the new grain formed is restricted in its growth by its neighbours so that the growth of some of them is stopped as they become entirely enclosed by the encroachment of those more favourably oriented (Bathurst, 1958).

Consequently, the size in the mosaic increases with distance from the original wall, and there will be a development of orientation, optic axes, and shape (Fig. 4.2) (Plates 4.5C and 4.6A).

Bathurst (1958) discussed the consequences of the mutual obstruction by adjacent growing faces in the production of phase intergranular boundaries. He argued that if the conditions are the same over the adjacent faces of the crystals then their growth rates are related by a constant. He mentioned that the line joining the two faces in a plane does not coincide with any particular crystallographic directions.

Bathurst (1958) also mentioned that the boundary migration is hindered by the presence of impurities and voids. The driving force is believed to come partly from differences in surface tension across intergranular boundaries growth occurring on the lattice with the higher surface tensions, and partly from the differences in elastic strain of adjacent grains.

In the Pendleside Limestone, examination of some thin sections revealed that fine-grained fabrics, once homogeneous, are now interrupted either by coarse mosaic or by syntaxial rims on skeletal fragments, mainly crinoid ossicles or echinoderm plates (Plate 4.6A).

iii) Syntaxial cement:- It has long been known that cementation around echino-derm debris is usually achieved by enlargement of the calcite crystals of the original fragment. This appears to have been observed first in hand specimen as early as 1826 by Hessel. In thin section the lattice continuity between the crystal of the detrital fragment and its overgrowth is shown by the fact that under crossed polars they extinguish as a single crystal. Sometimes when echinoderm debris is mixed with other skeletal fragments like peloids or ooids, the overgrowths from the echinoderm fragments are often relatively large

and appear to have swamped the polycrystalline pore-filling mosaic which developed around the other detrital components. Occasionally, the overgrowths are so large that they tend to enclose neighbouring polycrystalline fragments and their fringing cement. Evamy and Shearman (1964) described such a cementation as poikilitic. Bathurst (1958) considered this type of cementation as a special case and distinguished it from granular cementation because of its distinctive products, and it's importance in the fabrics of calcite-mudstone and siltstone, he coined the term "rim cementation" for such a process (Plate 4.6B and C).

Evamy and Shearman (1964) assigned the reason for such cementation to the force of crystallization which was more powerful in the overgrowth crystals than in crystals of cement origin. They provided a possible explanation for this kind of overgrowth and assigned it to the calcite scalenohedra which tends to elongate parallel to the c-crystallographic axis.

Richter and Fuchtbauer (1978) suggested that the replacement by ferroan calcite with preservation of the original structures can be used as a new criterion for identifying skeletons originally composed of high-magnesian calcite. This applies to bryozoa, rugose corals, echinoderms, many foraminifera, most ostracodes, red algae, and serpulids. On the other hand, skeletons originally composed of low-magnesian calcite were never replaced by ferroan calcite. They referred to the chemical instability of high-magnesian calcite as the driving force for the replacement by ferroan calcite.

The crinoid ossicles in the Pendleside Limestone Group often show ferroan calcite composition (Plate 4.6B) with increasing amount of iron towards the outer part of the crystal. This suggests, according to Richter and Fuchtbauer (1978) that the outer part of the cement crystals may originally have been high-magnesian calcite. The occurrence of

microdolomite rhombs in these fragments confirms a former high-magnesian composition

(Meyer and Lohmann, 1977) (Plate 4.9B and C). The outer part of each overgrowth,

however, shows sometimes a succession of zones of varying iron content, and the outlines

of these zones represent the shape of the overgrowth at the various stages of their

development (Plate 4.6B).

In some of the thin sections, the zones in the overgrowths are strongly serrated

where they have grown out from the articulating surfaces, that is in the c-crystallographic

axis direction. The axes of the serration are normal to the basal plane of each ossicle and

parallel to it's principal crystal axis. Around the sides of the same ossicle, the zones are

straight, and lie parallel to the sides of the ossicles, but at the same time parallel to the

principal axis. As a result of variation in the rate of growth of calcite with the

crystallographic direction, the zones are narrow at the sides of the ossicle and wide at

the serrated parts (Fig. 4.4A, B, C and D).

Cementation in lattice continuity involves not only the development of the over-

growth, but also the infilling of the canals. In some fragments no trace of the canal can

be seen because these canals were clean from any impurity (e.g. iron oxides) that mark

the boundary. Similarly, where the surface of the fragment is clean, little distinction

can be made between the original fragment and the overgrowth. When boundaries between

overgrowths are seen in thin section the crystals of the adjacent overgrowths are variable

in outline. The traces of the boundaries may be long and straight, saw-tooth or

occasionally curved. Often the trace of a boundary between two overgrowths changes

along it's length, being straight in one part, but serrated or curved in another (Fig. 4.4A,

B, C and D) (Plate 4.6B).

Buckley (1951) and Bathurst (1958) did not consider the boundaries as crystal faces,

but as compromised boundaries, because they are not parallel to the iron-bearing zones of the overgrowths but transgress them. The outline of the boundary between two over-growths will depend principally upon the morphological and crystallographic orientations of the fragment.

iv) <u>Pressure-solution:-</u> Pressure-solution is a well known process involving solution at contact surfaces followed by redeposition. Bathurst (1958, 1975) has discussed this phenomena with respect to the Carboniferous Limestones.

Two types of pressure-solution have been encountered in this work, these are:

A)   Grain to grain pressure solution:- The resultant fabric of pressure-solution is most clearly seen in the Pendleside Limestone Group in the coarse allochemical constituents because the structure of the allochemical constituents, e.g. ooids, peloids, are highly symmetrical (Plate 4.7A, B and C).

During the action of pressure solution in the Pendleside Limestone the point between the grains changes to surface contacts. It is the existence of these surface contacts that makes the resultant fabric relatively clearly recognisable.

Bathurst (1975) demonstrated that the form of the surface contact varies according to the different solubilities of the material on either side of the surface. He referred the pressure-solution to the strain between grain surfaces and to the solubility product constant. When a load is applied to the sediments, for example the overburden vertical pressure, the solubility product constant, $[Ca^{+2}][CO_3^{-2}]$, will be high in the grain surfaces and as a result, the ion activity product in the adjacent solution will likewise be higher. A concentration gradient will exist and solute ions will diffuse away

from the vicinity of the contact into the less concentrated solution occupying the adjacent voids. Near the unstrained surfaces, the solubility product is lower, and thus the influx of diffusing ions will lead to local supersaturation and consequent precipitation of $CaCO_3$ on these unstrained surfaces. Factors like grain orientation, sizes, shape and anisotropy of the crystal lattice will influence the preferential dissolution.

In any sediments composed of grains and water each grain is always elastically strained in the vicinity of an intergranular boundary, and this strain is enormously increased by the weight of an overburden. The strain is much more increased when it is accompanied by solubility. Ions from the lattice enter the solvent, in which there is a continuous concentration gradient, and diffuse away from the exposed intergranular boundary to regions of lower concentration. The lattice around such a point contact is dissolved and the convexities of the opposing grains are reduced. The form of the contact presumably changes from a single point to a number of very small points formed by the opposition of two minutely hummocky surfaces, some points being dissolved while others replace them. It seems that the surface contacts with no intervening, as distinct from point contacts, can never develop, because as soon as the smallest surface contact is formed the solvent is excluded from it and further change is not possible. Instead, solution continues at the junction between this interface and the solvent and so destroys it. Thus, although two opposing surfaces are maintained and enlarged, they must apparently always remain hummocky while pressure-solution is active.

Grain to grain pressure-solution can not take place after the precipitation of the second generation cement, or the final filling, simply because

the presence of this embracing material prevents the relative movement between the grains. Grain to grain pressure-solution can act after the precipitation of the first generation of cement, because the thin fringe of crystals does not prevent grain to grain movement, but sometimes the fringes themselves are involved in the pressure solution.

If pressure-solution acts after the precipitation of the second generation of cement, then it forms what is called a stylolite.

B)   Stylolites: Stylolites were identified as far back as 1828, when Keloden described stylolites sulcatus.

Stylolites are surfaces of complex interface in between two masses, each mass being columnar or irregular extension into the opposed mass. Stylolites differ from grain to grain sutured contacts only in scale; they transect the whole rock rather than isolated grains.

Bathurst (1975) mentioned that the initial surface at which dissolution begins is generally parallel to the bedding, though all orientations are known including surfaces perpendicular to the bedding. The zig-zag form of the surface is due to the lateral variation along the interface of solubility differences of the rock across the interface.

There is a relation between the stylolite development and porosity and permeability of the rock. Theoretically the migration of ions away from the dissolving surfaces can proceed by two paths; either in the stylolite surface film in a fully cemented rock, or away from the surface parallel to the linear stress axis, in a permeable rock. In many cases it has been observed that the porosity and permeability increase away from the stylolite surfaces. Bathurst (1975) explained the dissolution of the $CaCO_3$ during the

formation of stylolites by diffusion and redistribution of the $CaCO_3$ and

by the fluids in the rocks probably in a direction roughly parallel to the

stylolite surfaces.

An example of the pressure-solution stylolite is in Plate 4.8A, where

a calcisphere is crushed due to the exerted pressure and the dissolution of

the material in between the two masses of the rock body.

v) Post-depositional microcavities and internal deposition of sediments:- Secondary

cavities are formed after the deposition of carbonates, either by solution or internal

mechanical erosion. These cavities are filled with sediments either of the same material

that went into the solution or by some other type of sediments. These cavities can be

distinguished by their irregular shape and sometimes the difference in composition between

the host and the newly formed cavity fill; besides the contact will be sharp. They can also

be distinguished by their interruption of the once continuous fabric in the host rock and

a mass of oriented drusy mosaic filling in the cavity (Plates 4.8B, C and 4.9A).

4 2.3   Origin of porosity in the Pendleside Limestone Group

Porosity in carbonate rocks results from many processes, including those of

depositional and post-depositional origin. Several mechanisms appear to have been

particularly important in producing or changing of porosity and pore-size distribution in

the Pendleside Limestone Group.

Primary interparticle porosity is formed by deposition of a well-sorted calcareous

sand or calcareous sand size particles with sufficient rapidity to deposit particle on

particle and by winnowing of carbonate mud with little or no interstitial sediments.

Dissolution of interstitial mud in a calcareous sand can produce a microvuggy porosity

resembling interparticle pore space. Simple cementation by calcite destroys porosity and

pore size. Calcite cement appears to be especially common where the particles are monocrystalline, for example, crinoid fragments. Two groups of porosity type are observed in the limestones of the Pendleside Limestone Group: i) Primary porosity, and ii) Secondary vugs.

In addition dolostones also show well-developed intercrystalline porosity which will be discussed in a later chapter.

i) Primary porosity: Carbonate primary pore types in the Pendleside Limestone originate from the two common carbonate sediment types:

A)   Lime mud:- Lime mud is one of the common carbonate rock types in the lower succession of the Pendleside Limestone Group. The particles are mechanically, chemically or biochemically precipitated fine crystals originally composed of aragonite, now calcite. They sometimes contain very fine interparticle spaces in the magnitude of few microns, and occasionally retain relatively high porosity like their terrigenous clastic counterparts.

B)   Sand:- Some of the carbonate sediments in the Pendleside Limestone are deposited as well-sorted, texturally mature, sand size grains resembling grainstones or packstones (Plates 4.1A, B, C, and 4.2C). These sediments are deposited generally under conditions of sufficiently rapid water movement, for example, waves, tidal currents, which either removed the finer particles or transported them and selectively deposited the larger particles.

The nonskeletal particles, such as ooids and peloids, all fall under the sand category. Also the sand size and larger particles of whole or broken fossils, lumps of partially lithified contemporaneous sediments, and some fragments of older carbonate rocks fall under the same category. When free of mud, these carbonate sands have porosities and pore size

distributions similar to their well-sorted, terrigenous clastic equivalents. The carbonate sands are often poorly sorted. In fact, a complete physical gradation exists from sorted carbonate sands to those with a carbonate mud matrix between self-supporting sand size particles floating within mud, to mud with few sand size particles (Plate 4.2B). As a matter of fact, addition of the mud matrix reduces the porosity and pore size in primary sediments.

The rate of mud deposition is controlled by the rate of production of fine size carbonate particles or crystals and the ability of currents to selectively remove the mud from the site of deposition. At times production and deposition of particles is so rapid that the larger carbonate particles fall one on top of the other producing interparticle void space. This space may or may not contain mud. Examples of sand-size, texturally mature limestones are in the Hodder River section (100), the Rad Brook section, and section 400 on the Pendle Hill, all of which represent shelf-deposits (Plate 4.1A, B and C).

In contrast, basinal types of fine grained deposits in the Pendleside Limestone are represented in section PL + RW in the Salterforth area (Plate 4.8A and B).

ii) Secondary vugs:- The development of secondary voids larger than the normally expected interparticle voids, represents a separate group in carbonate diagenesis. Several mechanisms are important; some produce an interconnected vug network, and others contribute to pore volume but depend on associated interparticle or intercrystalline pore space for their interconnection.

A)   Carbonate dissolution:- Examples include dissolution of selected fabric elements, such as particular fossil fragments or parts of fossil fragments. In addition, selective dissolution of part of the carbonate mud matrix in a poorly sorted crinoidal or other carbonate sand can produce an interconnected vug network

resembling interparticle porosity. Examples of selective leaching in an echinoderm plate and replacement by silica is shown in Plate 4.6C.

B)   Fractures:- The development of open fractures represent a void-producing mechanism (Waldschmidt et al., 1956). The enlargement of such fractures by dissolution of carbonate host rock is observed in the Pendleside Limestone Group. Fractures other than voids, are subject to cementation as in Plates 4.2C, 4.3A and B.

4.3   The origin of ferroan calcite cement

It is well known that ferroan calcite can not precipitate directly from sea water because of it's low iron content and it is incorporated into the calcite structure in later stages of diagenesis. In present seas aragonite and high-magnesian calcites and to a lesser extent low-magnesian calcites are the major precipitated material. Many people think that this was the situation in the past seas and it is now known that aragonite and high-magnesian calcite, being both metastable, are transformed into generally sparry calcite and micrite respectively (Folk and Land, 1975) (Fig. 4.5).

In the Pendleside Limestone, the first cementing material in the pore solutions was generally high-magnesian calcite. Indications are:-

1)   The existence of microdolomite inclusions in the syntaxial overgrowths of the crinoids and echinoderm plates (Plate 4.9B and C). Lohmann and Meyers (1977) proposed that microdolomite was evidence for the former existence of high-magnesian calcites in the environment of deposition. Due to the metastability of the high-magnesian calcite, it dissolved differentially and reprecipitated as a second generation cement but with Fe^{+2} ions replacing

Mg^{+2} ions which are incorporated in the microdolomite structure.

2) The predominance of a high quantity of micrite which is the stable phase of the pre-existing metastable high-magnesian calcite: due to the metastability of the pre-existing high-magnesian calcite which constituted the primary cementing material of the Pendleside Limestone, the magnesian calcite was transformed into micrite. During the process of the gradual dissolution of the high-magnesian calcite into micrite, the reaction incorporated the iron, which stabilized the calcite and precipitated the ferroan calcite as the final cementing material and most stable one. The iron was incorporated gradually into the solution depending perhaps on the rate of dissolution of the high-magnesian calcite. This is why we tend to find the differential content of iron in ferroan calcite cements, and the increase in the secondary veins or vugs which represent a late stage of diagenesis.

Oldershaw and Scoffin (1967) distinguished two stages of cement in the Carboniferous Limestone in North Wales. They were able to demonstrate a positive relationship between the iron content and the presence of shale beds. The same phenomena is observed in the Pendleside Limestone. In the lower parts of the succession, thick beds of shale alternate with shaly limestones, and as we pass upwards the shale beds decrease in thickness and number, eventually disappearing in the uppermost part of the succession.

Examination of stained thin sections revealed that the abundance of ferroan calcite cement is greater in the lower part of the succession where there are thick beds of shale. There is a progressive decrease in the amount of ferroan calcite in the middle parts, where thinner horizons of shale beds alternate with the shaly limestone beds. In the upper parts of the Pendleside Limestone where shale horizons are scarce and the limestone-dolostone

beds are well-developed, ferroan calcite is relatively scarce.

The same iron content is observed where the limestone beds are partially dolomitized in the lower part of the Pendleside Limestone succession, where all the dolomite rhombs are ferroan dolomites, whereas in the uppermost part of the succession, the iron content is less and no ferroan dolomite exists, but only occasional iron oxides. Ferroan dolomite occurs only near the pore spaces and fissures.

An interesting analysis was carried out to visualize the iron content and its distribution throughout the Pendleside Limestone Group. Atomic absorption analyses of samples collected from Pendle Hill, Hodder River, and the Salterforth area revealed remarkable variation of this element throughout the Pendleside Limestone succession. The results of the atomic absorption were processed using SYMAP computer program (Appendix C). The resultant map in chapter five (Fig. 5.19) shows the concentration of the iron throughout the Pendleside Limestone succession in the forementioned localities. The iron increases in the lower parts of the succession but passing upwards the iron content decreases.

In the Slaidburn area the same process was applied and the resultant map (Fig. 5.24) shows fluctuation in iron concentration throughout the Pendleside Limestone Group; but there is a pronounced increase in the concentration of iron towards the west-southwest where the shales increase towards the basin. This phenomena will be discussed in detail in chapter five.

4.4   Authigenesis

4.4.1   Introduction: occurrence of authigenic feldspars and authigenic quartz in the Pendleside Limestone Group

During the petrographic examination of thin sections from samples obtained from the Pendleside Limestone Group, it was noted that well formed euhedral crystals of authigenic feldspars and authigenic quartz are well developed in the lower part of the succession rather than at the uppermost part of the succession. Authigenic grains are far more abundant than their detrital equivalent (Plate 4.10A, B and C). The authigenic feldspars almost completely disappear in the upper part of the succession but occasionally authigenic quartz is present. Furthermore the authigenic feldspars increase where the shale beds are well-developed and they are almost all concentrated near the bedding planes in between the limestones and shales.

One of the earliest recorded identifications of authigenic feldspars was made by Drian (1861). He noted tiny well formed feldspar crystals which contained some inclusion of opaque material. From the manner in which the crystals were disseminated throughout the rock, he inferred that they developed while the rock was in the process of formation and not as a result of subsequent metamorphism.

Rose (1865) described a peculiar "fourlings" generally known as "Roc Tourné" twins. He was considered to be the first to describe the crystals of authigenic feldspars in detail. At about the same time Lory (1861) examined the same type of crystals and arrived at a similar conclusion regarding the origin of the albite crystals. Several Italian writers, among them De Stephani (1879) and Spezia (1880) have described albite crystals that occurred in the limestones of the Italian Alps and Apennines. Baskin (1955) discussed the occurrence of alkali and plagioclase feldspars including their physical and optical

mineralogy. He noticed the association of the sodic feldspars with dolomitization and/or recrystallization of the host rock, but he didn't explain what the relation was between dolomitization and/or recrystallization and the formation of the authigenic feldspars. Swett (1968) in his discussion of the lower Cambrian "Fucoid Beds" of north-west Scotland referred to the exceptionally high content of potash feldspars. He gave an account of their petrologic texture and origin. Kastner (1971) also discussed in detail the occurrence of authigenic feldspars in marine limestones and dolostones. She discussed the chemical, physical, and the crystallographic properties of the authigenic feldspars concluding that the chemical environment of formation of authigenic albite does not necessarily differ appreciably from the environment of authigenic microline. Her calculations, which were based on ion exchange and thermodynamic data from the literature show that the K/(K + Na) ratio in the fluid phase in equilibrium with both albite and microcline at 100°C approximately equal to the K/(K + Na) ratio in seawater.

4.4.2   Authigenic feldspars and quartz in the Pendleside Limestone Group

Petrographic examination of the feldspar crystals show that they are exclusively sodic feldspars (albites). This is confirmed by the X-ray diffraction which has been used to identify the insoluble residues, including clay minerals, of the limestone specimens. Samples of limestone were treated in 10% HCl to dissolve the carbonates and the residue dried on a glass at room temperature ready to be examined by the X-ray diffraction method. The results of the X-ray analysis for the limestones are shown in Figs. 4.6A, B, C and D, the minerals identified being quartz, albite, kaolinite, and illite.

In associated shale samples the following minerals were identified: calcite, albite, kaolinite, quartz and occasionally illite (Fig. 4.7A, B, and C). Four major criteria are used for distinguishing authigenic grains:

(a) Crystal habit - All authigenic grains are euhedral with pinacoidal faces or tend to show a euhedral shape (Plate 4.10A).

(b) Textural relationship - As established by microscopy, authigenic feldspars and authigenic quartz replace fossils, cut across peloids (Plate 4.10C) and fill cavities and contain rock inclusions.

(c) Twinning in authigenic feldspars - Authigenic albites are either untwinned, twinned after the albite law as contact twins, or twinned after the cross-carlsbad law as penetration twins, each consisting of two individuals.

(d) Inclusions - carbonate inclusions and sometimes minute ferroan dolomite rhombs are present in all the authigenic grains. The composition of the inclusions and the rock matrix are identical as established by the microscopic examination (Plates 4.10B and 4.11A).

4.4.3 Geochemical environment and the diagenetic stage of the formation of authigenic quartz and authigenic feldspars

In the authigenesis of the feldspars and quartz the following were observed:-

1. The total amount of authigenic feldspars present in the rocks studied is very small ($<5\%$).

2. The abundance and development of authigenic feldspars is concentrated in the lower part of the succession of the Pendleside Limestone where thick beds of shale occur. The feldspars are only poorly developed in the upper parts of the succession.

3. Authigenic quartz is equally abundant throughout all the succession of the Pendleside Limestone Group.

4. The concentration of the authigenic feldspars near bedding planes and contacts between the shale and limestone or shaly limestone.

5 Albite is the dominant authigenic feldspar phase present in the Pendleside Limestone Group.

6. The occurrence of ferroan and non-ferroan microdolomite rhombs attached to the wall surfaces of the authigenic feldspars and authigenic quartz crystals, where no regional dolomitization is observed in the matrix of the same rock.

The probable explanation for the origin of the aluminium silicate in the authigenic albites is as follows. Since it only occurs in the lower part of the Pendleside Limestone succession in proximity to shale beds it is most likely that the clay minerals in the shale beds, namely kaolinite and illite, were the main source for the aluminium silicate. The X-ray diffraction of some shale samples show high content of kaolinite and occasionally some illite as in Fig 4.7A, B and C. The major source for silica used in the crystal- lization of the authigenic quartz, however, is more likely to be the dissolved siliceous spicules which provided the silica supply for chertification of the limestones. This is discussed in chapter six.

The exclusive occurrence of the sodic feldspars (albite) suggests that the sodium is provided from seawater. Kastner (1968) stated that the amount of sodium in 9 mm^3 of seawater is equivalent to the amount of sodium in an albite crystal 1 mm in diameter. Kastner (1971) suggested that albites are more likely to form at temperatures higher than 25°C or in equilibrium with waters enriched in silica and alkalies relative to seawater. The latter assumption is more likely to happen because the medium is likely to be saturated with silica due to the dissolution of the siliceous spicules, and the occurrence of aluminium silicate in the shales.

Saturation and enrichment in respect to alkalies, e.g. Na^+, K^+ can be explained as follows:-

During sedimentation when porosity was high enough, seawater containing Na^+, K^+ and Mg^{+2} was trapped in the pore spaces especially when burial was fast enough due to tectonic influences. Due to the exerted overburden pressure on the trapped seawater, saturation is brought about in respect to the alkalies, and magnesium. Since Na^+ ions have higher ionic activity than K^+ ions (Periodic table) it is more likely that it exclusively reacts with aluminium silicates that are concentrated in the clays in the shale beds and the contacts of the limestones with shale, and eventually forms authigenic sodic feldspars.

As for the Mg^{+2} ions they react with the $CaCO_3$ and Fe^{+2} ions in a restricted environment to form the ferroan microdolomites (Plate 4.1A and B). If seawater percolated freely in the sediments which contained reasonable amounts of clay, the distribution of the authigenic feldspars would have been uniform throughout the limestone units and the shale units if not the whole Pendleside limestone succession. In addition proper large dolomite rhombs would have been dispersed throughout the sediments and rock matrices, and no microdolomites would have formed. The textural fabric of the authigenic feldspars suggests that the solutions dissolved the calcium carbonate and replaced them and reprecipitated the albites and ferroan microdolomites.

Some of the authigenic feldspars are decomposed into authigenic clays in a reducing environment containing Fe^{+2} ions. Whereas the authigenic quartz crystals are still stable (Plates 4.11C and 4.12A, B and C).

4.5   Geochemical aspects of carbonate diagenesis

Details of lithology from different sections are mentioned in the stratigraphy

chapter 2, but a summary of the lithologies of the Pendleside Limestone Group will be adequate here for the geochemical interpretation of data.

The Craven Basin in the Dinantian times trended northeast-southwest with an irregular outline and an asymmetrical cross section as can be judged from the isopach map of the Pendleside Limestone Group in chapter 2 (Fig. 2.10). Different parts of the succession with respect to the basin are exposed, for example in the Hodder River section (100) (Fig. 2.7A), a complete succession of the Pendleside Limestone is seen to be gently dipping northwest. The succession is composed of an alternation of thin beds of shale (30 - 80 cm) in thickness and shaly limestone in the lower part of the succession passing upwards to thinner beds of shale and more massive layers of shaly limestones, and at the uppermost parts of the succession, the shales completely disappear and only limestones, dolomitic limestones and dolostones are present. Chert layers alternate with the limestone, and the cherts are well developed in the upper parts of the succession.

In sections 200 and 300 to the northwest of the Clitheroe area, near Slaidburn (Fig. 2.8) the Pendleside Limestone is poorly developed, and the main lithologies are limestones and occasional dolomitic limestones with very thin shale horizons at the bottom of the succession. Whereas in sections 600, 700 and 800 in the same area (Fig. 2.8), the succession is more shaly with occasional development of limestones.

On the Pendle Hill sections (400 and 500) the succession is composed of thick beds of shale (200 - 300 cm) in thickness in the lower part of the succession alternating with thin shaly limestone and passing upwards to shaly limestones with a decrease in the shale thickness and in the uppermost part of the succession the beds are limestones and dolo-stones with no shale beds. The rest of the sections on the Pendle Hill (1200, 1300, 1400 and 1500) are intermittently exposed and complement each other. They are mainly shaly limestones, limestones and dolostones.

In sections 900, 1000 and 1100 north of Clitheroe (Fig. 2.8), the exposures complement each other and they are mainly shaly at the bottom of the succession passing upwards to more massive layers of limestones, partially dolomitized in some parts.

All of the mentioned sections generally have an alternation of shale and shaly limestone of basinal type at the lower part of the succession, denoting that the basin was relatively deep at the beginning of deposition of the Pendleside Limestone Group, but passing upwards, shelf deposits (limestones) are more evident.

The distribution of the carbonates (limestones and dolostones) as   is evident in the isoplith map of the carbonate (Fig. 2.12), denote that all the previously mentioned sections fall on the flanks of the Craven area. and constitute shelf deposits.

In section RW+PL in the Salterforth area, which is closer to the central part of the basin, the lithology is mainly thick beds of shale (3 - 4 m in thickness) and shaly limestones of basinal type. The isoplith map of shale (Fig. 2.13) shows concentration of the shales in that part of the basin.

Geochemical analysis of samples collected from all of the mentioned sections show a pattern of concentration of elements like Al^{+3}, Na^+, and K^+ according to the lithological distribution in the basin. Where thick beds of shale occur, clays increase in concentration and in turn the Al^{+3}, Na^+ and K^+ ions increase in concentration.

Atomic absorption spectrophotometry was carried out on samples of limestones and shales from different sections (procedure in Appendix B). Concentrations in parts per million for Al^{+3}, Na^+ and K^+ ions are shown in Table 4.1 for section 100 in the Hodder River Valley. The analyses show that ppm values for Na^+, Al^{+3} and K^+ are relatively low compared with the analysis of samples collected from a more basinal type succession

such as section PL+RW (Table 4.9). These show higher ppm values for Na^+, K^+ and Al^{+3} and a higher concentration of clay minerals as indicated by the X-ray diffraction analysis of samples of limestone and shale.

In section 400 the ppm values for Na^+, K^+ and Al^{+3} (Table 4.4) are higher at the lower part of the succession where thick beds of shale occur, and clay content is high, rather than the upper parts, where the shales are absent. The ppm values in sections 1200, 1300 and 1500 are relatively low due to the absence of shale in these sections. Also the dolomitization and silicification processes have obscured the original features of the deposits. Tables 4.6, 4.7 and 4.8 respectively show relatively low ppm values for the mentioned elements.

As for the northern and northwestern sections the ppm values for Na^+, K^+ and Al^{+3} (Table 4.2 for section 200) (Table 4.3 for section 300) show relatively low values because of the absence of shale and thus low clay mineral content in the succession. In section 800 (Table 4.5) the ppm values increase for Na^+, K^+ and Al^{+3}, because of an increase in the shale content in this central region of the basin.

The highest concentration of Na^+, K^+ and Al^{+3} ions occurs in sections PL+RW (Table 4.9), which is located in the central part of the basin where the lithology is mainly shale and shaly limestones of basinal type. X-ray results show an increase in kaolinite and illite throughout the succession (Fig. 4.7C).

The ppm values for the mentioned elements were processed by computer program (SYMAP); details of this program are given in Appendix C. SYMAP is a shade drawing program that shades and distributes the mentioned elements vertically and laterally throughout the succession according to their concentration (ppm) values.

The aluminium distribution in sections 100, 400, 1200, 1300, 1500 and PL+RW show a considerable vertical and lateral variation throughout the Pendleside Limestone (Fig. 4.8). The Al^{+3} values show an increase (19691 ppm - 27895 ppm) in the eastern part of the area (section PL+RW) but passing westwards the ppm values fall considerably. The Al^{+3} concentration is higher in the lower part of the succession and decreases upwards, although there is considerable fluctuation in the vertical distribution.

If a comparison is made between the pattern of the Al^{+3} ppm concentration distribution and the shale and limestone distribution vertically and laterally throughout the Pendleside Limestone succession, we can draw a noticeable congruency in the positive relation of the Al^{+3} ion and shale distribution.

To the north and northwestern parts of the Clitheroe area and around sections 200, 300 and 800) the Al^{+3} ppm concentration shows a noticeable increase towards the west and south, where the shale increases (Fig. 4.9). The Al^{+3} ppm values show a decrease to the east and especially the upper parts of the succession in the eastern sections. The general trend of the map shows an alternation (periodical) increase and decrease that corresponds to the maximum deposition of the shales.

The sodium concentration imitates the Al^{+3} concentration in pattern and shows a concentration that coincides with the shales and especially with the authigenic feldspars in the lower part of the succession. In Fig. 4.10, which is the vertical and lateral variation map for Na^+ in sections (100, 400, 1200, 1300, 1500 and PL+RW), the Na^+ shows a remarkable increase in section PL+RW which is a more basinal type of deposit, and a decrease to the west represented by section 100, which is mainly limestones and dolomitic limestones with occasional shale.

In sections 400, 1200 and 1300 the Na^+ (ppm) is concentrated in the lower part of

the succession in the range of 1647 ppm – 4618 ppm and decreases in concentration at the upper parts where the lithology is mainly limestones and dolostones with no authigenic feldspars at all. In the lower parts however, large euhedral crystals of authigenic albite are abundant.

In sections 200, 300 and 800 the Na^+ concentration (Fig. 4.11) increases in section 800, which contains shale beds and an abundance of authigenic feldspars rather than sections 200 and 300, which are nearer the basin margin and devoid of the authigenic feldspars.

The K^+ ppm values in sections 100, 400, 1200, 1300, 1500 and PL+RW (Fig. 4.12) and in sections 200, 300 and 800 (Fig. 4.13) show a similar pattern of distribution to the Al^{+3} ions vertically and laterally throughout the Pendleside Limestone succession.

In conclusion the distribution maps for Al^{+3}, Na^+ and K^+ show a remarkable congruency with the lithological distribution of the shales vertically and laterally throughout the Pendleside Limestone Group. These elements show a noticeable increase where the shales and clays increase thus providing important evidence for the source of ions which formed the authigenic feldspars.

4.6 Discussion and conclusions

The history of events regarding the influence of pore solutions and the environment of deposition and later alteration, e.g. cementation and replacement, can be drawn from the fabrics, textural and compositional variation of the limestones and dolostones in the Pendleside Limestone Group. These reveal a great deal of diagenetic alterations.

Formation of first generation iron-free calcite cement was contemporaneous or

shortly followed deposition of the sediments. These calcite cements were probably metastable aragonite and high magnesian calcites. Evidence confirming the former presence of higher magnesian calcite are the microdolomite inclusions in crinoid stems and echinoderm plate overgrowths (Plate 4.9B and C) (Meyers and Lohmann, 1977).

The pore spaces were still open permitting large volumes of pore fluids to percolate and influxes of freshwater extended and created brackish water zone. This created favourable conditions for dolomitization which was brought about in zones of brackish water as will be discussed in a later chapter. Evidence confirming the influx of fresh water in large volumes, and the prevalence of an open system mechanism, is the low concentration of Sr^+ and Na^+ ions (Kinsman, 1969).

Textural relationships of dolomite rhombs and allochemical grains (dolomite rhombs could apparently grow on free surfaces of allochems) suggests relatively early diagenesis. Second generation ferroan calcite cement took place contemporaneous with and after dolomitization because the ferroan calcite cement needs a reducing environment to be deposited (Richter and Fuchtbauer, 1978). The second generation cement could not have taken place before dolomitization due to the following reasons:-

1) The second generation cements block the whole pore spaces; since this will restrict the percolation of dolomitizing fluids, it seems likely that dolomitization could have taken place more easily prior to second generation cement.

2) The dolomitization mechanism (mixed water type) suggests an oxidizing environment in which the dolomitization took place. If the dolo-mitization took place after the second generation cement, it would have oxidized all the iron in the ferroan calcite cement. This is not the case in the Pendleside Limestone since most of the ferroan calcite

cement is not oxidized.

3)   Textural relationship of the dolomite rhombs and allochemical
     components suggests the earlier development of these rhombs before
     pore spaces were blocked with ferroan calcite cement (Plates 4.5B
     and 4.10C).

4)   The formation of authigenic grains, e.g. feldspars and quartz was
     contemporaneous with the dolomitization as suggested by their
     textural relationship (Plates 4.10A and C).

In conclusion, the formation of first generation iron free calcite cement was followed
by dolomitization as a consequence of the influx . of fresh water from land areas to be
mixed with trapped seawater thus forming the brackish water zone. Dolomitization
proceeded in a phreatic lens of brackish water and consumed the magnesium available in
the high magnesium-calcites and in trapped seawater. Contemporaneous with the dolo-
mitization process, authigenic feldspars and quartz were formed as suggested by the
coexistence of both dolomites and authigenic grains in some of the samples.

Second generation ferroan calcite cement took place during and after the dolomiti-
zation episode in a reducing environment and the iron source was evidently clay minerals
in interbedded shale horizons in the lower parts of the Pendleside Limestone succession.

Chapter Five

DOLOMITIZATION OF THE PENDLESIDE LIMESTONE GROUP

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Chapter Five

DOLOMITIZATION OF THE PENDLESIDE LIMESTONE GROUP

5.1 Introduction

Voluminous work has been done in recent years on the process and problems of

dolomitization (Fairbridge, 1957; Friedman and Sanders, 1967; Zenger, 1973). A recent

review on the subject has been presented by Folk and Land (1975).

Later work regarding dolomitization in the Lower Carboniferous was carried out

by Bhatt (1976) who discussed the Dinantian limestones in South Wales and suggested

that the dolomitization took place under hypersaline conditions by a "seepage-reflux"

mechanism. Al-Hashimi (1972) used the scanning electron microscope to study the

dolomitization process in the Lower Carboniferous of the Northumberland Basin in

Northern England. He discussed the textures and porosities created by this process and

also discussed the source of the carbonates and the role of clay minerals in dolomitization.

However, very little work has been accomplished on the dolomitization process and its

mechanism in the Craven Basin generally, and up to the present time, little

is known of the dolomitization in the Pendleside Limestone Group.

Hind et al. (1901) briefly referred to the dolomitization in the Pendleside

Limestone and noted that some of the dolomite rhombs were well-developed and

stained or rimmed with iron oxide; also in the silicified horizons, the dolomite rhombs

are inconspicuous as ill-defined bodies floating in the silica matrix.

Earp et al. (1961) in the Clitheroe memoir described the Pendleside Limestone

as hard, compact, dark grey cementstones and noted that they were dolomitized and/

or silicified in some parts. The dolomites were thought to be secondary and of late diagenetic origin.

The work involved in this thesis discusses the effects of dolomitization vertically and laterally throughout the Pendleside Limestone Group, and also the mechanisms responsible for this diagenetic process. The techniques employed in the study included detailed thin section petrography, and scanning electron microscopy (SEM), and also X-ray diffraction (XRD) in order to determine the mineralogical composition of lime-stones and dolomitic limestones and dolostones. Atomic absorption spectrophotometric analysis was used on selected samples to determine the variation of some elements: strontium, iron, manganese, silicon, aluminium, sodium, and potassium at various horizons. Electron probe microanalysis (EMP) of polished thin sections was used to determine dolomite composition and the compositional variation in single dolomite crystals.

Characteristic results were established from the above mentioned analyses regarding the regional pattern of the dolomite distribution, and the mechanism respon-sible for the dolomitization process.

5.2 Field and laboratory criteria for dolomite recognition

Three criteria were most effective in the recognition of dolostones and dolomitic limestones in the field.

i) Colour distinction: most of the dolostone beds are characterized by a creamy-yellowish colour on freshly fractured surfaces. Fracture surfaces are sometimes brownish-red in colour because of iron oxide staining. The dolostone beds contrast very characteristically with the adjacent pale grey or dark grey limestone beds with

which they alternate.

ii) <u>Textural appearance</u>: most of the dolomite beds have coarsely crystalline texture. The size and shape of the dolomites are distinctly recognizable with the use of a hand lens. This is in marked contrast to the textures of the limestones which are finely crystalline and micritic.

iii) <u>Fossil content</u>: fossils are scarce or absent in the dolomitic limestone and dolostone horizons. Neither macrofossils nor microfossils are found in thin sections of completely dolomitized limestones. Use of the forementioned field criteria revealed that dolomitization increases towards the top of the Pendleside Limestone Group.

Over five hundred specimens were collected from the studied sections of the Pendleside Limestone Group. From these, thin sections were prepared and stained using the combined stain method of Dickson (1965) (Appendix A). Dolomites do not react with the stain and remain colourless. Ferroan dolomite stains a turquoise colour with the tone of colour varying in proportion to the amount of iron present (Plate 5.1A).

Petrographic examination of thin sections revealed that the majority of the dolomites are associated with, and restricted to the coarse grained lith ologies which originally were texturally mature. However, not all the peloidal limestones or bio-sparite horizons are dolomitized, and it is clear that the process has been highly selective in places. The proportion of dolostone in the Pendleside Limestone Group increases towards the top of the Group such that the upper parts are in places completely dolomitized. This upward increase in the amount of dolostone is closely associated with a reduction in the amount of shale and an increase in the grain size of the allochemical constituents of the limestone.

Ferroan dolomitic limestones are restricted to the lower third of the Pendleside

Limestone Group, adjacent to, and alternating with the thick shale beds (Plate 5.1A).

The iron, in the form of Fe^{+2} is mainly in the lattice of dolomite crystals and this is an

important feature of the lower part of the Pendleside Limestone Group. By contrast, the

amount of iron in the upper parts is much less and is not generally associated with the

dolomite lattice. Here non-ferroan dolomites are characteristic. These may be

intimately associated with iron oxides which gives individual dolomite rhombs a

distinctly zoned appearance. The iron is restricted to pores and microfractures in the

rock and coats dolomite rhombs. It also forms the inner core of rhombs (Plate 5.1B and

C).

5.3 Vertical and lateral distribution of dolomite in the

Pendleside Limestone Group

In order to characterize the vertical and lateral distribution of dolomite, the

application of XRD analysis of powdered rock samples was undertaken for all the

specimens. Each sample was analysed under the same conditions using a Phillips PW

1130/40 with CuKα, Ni-filtered radiation at 1°2θ/minute. The XRD analysis was

consistent with the thin section petrographic examination, and the constituent minerals

detected were calcite, dolomite, and quartz. The results were also used to calculate

the calcite:dolomite ratio of each sample. It is possible to distinguish the distribution

pattern of the dolomitization through thin section examination of rock samples, espe-

cially when the staining technique is applied. But when dolomitization intensity is

low (10%) it becomes hard to distinguish properly the effect of dolomitization especially

in fine grained rocks. Furthermore in partially dolomitized limestones the absolute

estimation of calcite and dolomite is extremely difficult using petrography alone.

Therefore XRD analysis has been used for all quantitative determinations.

The peaks of calcite at 29.43° 2θ (d Å = 3.034) CuKα₁, and dolomite at 30.98 2θ CuKα₁ (d Å = 2.886) are chosen because they have the greatest intensity for calcite and dolomite respectively, and are relatively free of interference from peaks of other minerals that may occur in small amounts in carbonate rocks; they are also close together, thereby facilitating accurate measurement. The peaks are measured for height (intensity) directly on a diffractogram tracing (Fig. 5.1) and measurement of the background intensity is determined by extrapolating the background line underneath the respective peaks (Royse et al., 1971).

Royse et al. (1971) confirmed that the Tennant and Berger (1957) curve (Fig. 5.2) can be used to estimate a composition within ± 6% dolomite with 95% confidence.

Gulbranden (1960) gave the following relationship

$$x = \frac{Y - 0.3921}{0.7885}$$

where $x = \log 100 \dfrac{\% \text{ calcite}}{\% \text{ dolomite}}$

and $Y = \log 100 \dfrac{\text{peak height of calcite} - \text{background calcite}}{\text{peak height of dolomite} - \text{background dolomite}}$

He used a plot of logarithms of the ratios so that peak-height ratio plotted against the percentage would be a linear function. Royse et al. (1971) suggested, however, that the Gulbranden (1960) relationship cannot be recommended and the graph in Fig. 5.2 is preferable. They recommended the use of their relationship

$$\frac{\text{dolomite}}{\text{dolomite} + \text{calcite}} = 0.010 \text{ weight } \% \text{ dolomite} - 0.023$$

as being more accurate. They concluded that the X-ray peak height provides the most rapid and precise procedure for determination of calcite and dolomite.

The X-ray diffraction of samples collected from the Hodder River section (100) (702339) revealed horizons with appreciable dolomite content. The amount of dolomite ranged from 4.1 wt. % to 49.4 wt. % dolomite using Royse et al.'s method. Fig. 5.3 shows the wt. % dolomite throughout the Pendleside Limestone Group at the Hodder River section (100) (702339).

On Pendle Hill and in the Rad Brook section (RB) (788428) many horizons of dolomitic limestones and dolostones are encountered (Fig. 5.4). The lower horizons are thin dolomitic limestones and the dolomite intensity ranges from 3.7 wt. % to 15.0 wt.% dolomite. The upper horizons show an intense zone of dolomitization where the intensity ranges up to 100.0 wt.% dolomite. The zones of intense dolomitization are correlated with the remaining sections on Pendle Hill.

In section 400 (787427) on Pendle Hill, six horizons of dolomitization can be distinguished, the lower three of which range in intensity from 3.1 wt. % to 11.3 wt. % dolomite (Fig. 5.5). The succeeding horizon has an intensity as high as 100.0 wt. % dolomite, and the remaining horizons range in intensity from 8.0 wt. % to 10.0 wt. % dolomite. In section 500 (787426) on Pendle Hill, seven horizons of dolomitization are distinguished which can be correlated with the Rad Brook (RB) section on Pendle Hill. The remaining sections on Pendle Hill, namely section 1200 (779415), S. 1300 (770408) and S. 1500 (761393) show high intensities of dolomitization; all these sections constitute and expose only the upper part of the Pendleside Limestone Group. As for section 1400 (768400), the intensity of dolomitization range from 7.7 wt. % to 34.4 wt. % dolomite. This section includes the middle part of the Pendleside Limestone Group.

Figures 5.6, 5.7 and 5.9 show the intensities of wt. % dolomite for sections 1200,

1300 and 1500 respectively and Figure 5.8 shows the wt. % dolomite in section 1400.

In the Slaidburn area, in section 200 (723503), three horizons of dolomitic

limestone can be distinguished, one of which is 100 wt. % dolostone (Fig. 5.10). In

section 300 (708501) and section 700 (714497) only one horizon of dolomitic limestone

is distinguished. The wt. % dolomite ranges from 16.0 wt. % to 33.3 wt. % dolomite

(Fig. 5.11 and 5.12 respectively). In section 600 two horizons of dolomitic limestone

can be distinguished, these range in intensity from 4.2 wt. % to 14.9 wt. % dolomite

(Fig. 5.13). The exposures in the Slaidburn area are intermittently exposed and poorly

developed, hence it is rather hard to distinguish the dolomitization episodes in this

area confidently.

In the Holden area, and in section 1100 (772494) which is intermittently exposed,

seven horizons of dolomitization can be distinguished.   The wt. % dolomite

range from 7.0 wt. % to 19.3 wt. % dolomite, whereas in the remaining section (1000)

(773503) and section 900 (765501) no significant dolomitization can be distinguished.

In the Salterforth area in section PL+RW (889458) six distinct horizons of

dolomitization can be distinguished, all range from 0.5 wt. % to 49.0 wt. % dolomite

(Fig. 5.15). These horizons resemble the horizons in the Rad Brook on Pendle Hill in

number but not in intensity. The Pendle Hill sections have higher intensities.

In the Lothersdale area, in section 1700 (939445) which is intermittently exposed,

only one horizon of dolostone (100 wt. % dolomite) is encountered at the lower part of

the exposure (Fig 5·14).

Ten horizons of dolomitization can be distinguished in the completely exposed

sections on Pendle Hill and in the Hodder River section (100). This suggests ten episodes of dolomitization that took place during periods of maximum limestone deposition prior to sea-floor subsidence. The dolomitization intensities increase towards the south and decrease northwards and eastwards towards the basin.

The wt. % dolomite values in Figs. 5.3, 5.5, 5.6, 5.7, 5.9 and 5.15 were processed using the computer program SYMAP (Appendix C). The resultant map in Fig. 5.16 shows the vertical and lateral variation of dolomite in sections 100, 400, 1200, 1300, 1500 and PL+RW. The study area is separated into two parts using SYMAP, the Slaidburn area being the first part and Pendle Hill, Hodder River, and Salterforth area being the second part. The reason for the separation of SYMAP values is discussed in Appendix C.

The dolomite percentage increases in sections 400, 1200, 1300 and 1500 (located on Pendle Hill) to values as high as 100.0 wt. % dolomite. To the west in the Hodder River section (100), the percentage of the dolomite falls to a range of 20.0 - 30.0 wt. % dolomite, and the percent values show regular cyclicity in the dolomite percentage throughout the succession.

To the east, and in section PL+RW, the dolomite percentage increases in the upper parts of the succession and decreases downwards. The values again show cyclic fluctuation in the percentage values of dolomite. The values of Figures 5.10, 5.11 and 5.13 were processed using the computer program (SYMAP). The map in Fig. 5.21 shows an increase in the percent dolomitization towards the northeast and a wedge out of the dolomite to the south and southwest (towards the basin) is evident. The sections in the Slaidburn area are intermittently exposed and it is rather hard to distinguish the episodes of dolomitization in the area. The configuration of the wedging out of the dolomite in

Figure 5.21 suggests that the dolomitization process was initiated from the north of the mentioned area.

5.4 Petrography of dolomitic limestone and dolostone horizons

Petrographic examination of the dolomite horizons revealed that there is a remarkable textural and compositional variation regarding the dolomite rhombohedrons throughout the Pendleside Limestone Group.

On Pendle Hill, the type locality of the Pendleside Limestone Group, in the lower part of S. 400 (787427), the dolomite rhombs show well-developed crystals of ferroan dolomite (Plates 5.1A and 5.2A). The rhombs display a hypidiotopic poikilotopic fabric (Friedman, 1965). They have a uniform distribution of iron throughout them and the iron is chemically incorporated in the dolomite lattice. The rims of the dolomite rhombs show corrosion-like features at their edges due to the effects of solutions as in Plate 5.2A. These rims are sometimes with iron oxide. The rhombs show overgrowth stages and sometimes the inner stages of the overgrowths are stained with iron oxide. The size of the rhombs is relatively smaller in the lower parts of the succession than in other localities such as S. 1200 (779415) and S. 1500 (761393). In the upper parts of the succession in the Pendleside Limestone Group on the Pendle Hill S. 400 (787427), the rhombs show a relatively larger size compared with the lower parts of the succession. They are described as being idiotopic fabric and poikilotopic in their mutual relationships with the siliceous matrix. The iron is occasionally incorporated chemically in the dolomite composition, but the iron oxide coats the rims and fissures in the rhombs (Plate 5.1B). The rhombs show a perfect rhombohedral shape and the rims are perfectly preserved and well-developed. Occasionally the rhombs in the upper part of the mentioned section show overgrowth stages coated with iron oxide rims at every stage.

Further south on Pendle Hill, the upper part of the Pendleside Limestone Group is exposed in section 1200 (779415) and the dolomitization is more extensive in this section than in the previous section. The dolomite rhombs being larger in size are well-developed and form perfect euhedral crystals. They display an idiotopic porphyrotopic fabric compared with the dolomite rhombs in the lower part (Friedman, 1965). The rims are sharp and perfectly preserved, and some of them are coated with iron oxide (Plate 5.2B). Stages of overgrowth are evident in the lower part of the succession, where each stage is rimmed with iron oxide. There are some rhombs that do not show overgrowth stages in the upper parts of the succession, but have a cloudy core (Plate 5.2C). The core of the rhomb is coated with iron oxide which clears towards the outer zones of the overgrowth. It is noticed in this section that ferroan dolomites disappear and only iron-free dolomites exist.

In section 1500 (761393) which is located at the extreme south of the area on Pendle Hill, the dolomitization is most extensive relative to other sections. The dolomite rhombs are perfectly developed and are idiotopic in terms of fabric as in section 1200 (779415). The rims are well-preserved and coated with iron oxide in the lower part of the succession, which also shows stages of overgrowth rimmed with iron oxide at each stage (Plate 5.3A). The stages of overgrowth are evident in Plate 5.3B, and an outer zone of iron-free dolomite is well-developed. The zoning of iron oxide in the dolomite rhombs remarkably follows the core of the rhomb in almost every dolomite crystal. Ferroan dolomite was introduced later to these dolomitized zones as indicated in Plate 5.3C, in which the ferroan dolomite is forming only the outer parts of the rhombs, whereas the inner core is iron oxide stained. Some of the early formed large size rhombs in Plate 5.3C have ferroan dolomite zones on the rims adjacent to the pore spaces, whereas on the other side of the rhomb, no ferroan dolomite zones are observed.

In the Hodder River section (100) (702339), the dolomitization is not so extensive as in section 1500 (761393). The dolomite rhombs are well-developed in shape and size and display an idiotopic poikilotopic fabric as in Plate 5.4A and B. Almost all of the rhombs are ferroan dolomite, in which the iron is chemically incorporated and uniformly distributed. No zoning is observed but only occasional iron oxide coating of the rims is evident. The solutions had some influence on the rims of the rhomb as is evident in Plate 5.4B. No cloudy core is observed in the rhombs compared with the Pendle Hill sections. Higher up the succession in the Hodder River section (100) the dolomitization had little effect on the limestones and only a few small size rhombs can be observed developed at the walls of the cavities and pore spaces (Plate 5.4C). Neither ferroan dolomite nor iron oxide coating of the rims is observed in the upper parts of the succession in the Hodder River section.

In the Slaidburn area, nearly all the sections show little or no sign of dolomitization except in a few horizons where very little dolomitization (7.0 - 10.0 wt. % dolomite) occurs in the beds. No well-developed rhombs of dolomite are observed in these horizons. All the limestones are fine grained micritic limestones.

In the Holden area near Bolton by Bowland, especially in S. 1100 (772494), only few horizons of dolomitic limestones (5.0 - 11.0 wt. % dolomite) are observed. No well-developed rhombs are found, and all the limestones in the dolomitized horizons are fine grained recrystallized and/or dolomitized micrites.

In the Salterforth area, section PL+RW (889458), no extensive dolomitization occurs. The average dolomitization ranged in between 10.0 - 20.0 wt. % dolomite), although many horizons are differentially dolomitized. No well-developed dolomite rhombs are observed, but a few ferroan dolomite rhombs, very minute in size, developed

on the walls of authigenic feldspars and quartz (Plate 4.11A, B and C). Occasionally the matrix of the rocks is dolomitized but on a very small scale.

In the Lothersdale area, particularly in S. 1700 (939445) only the upper part of the Pendleside Limestone Group is exposed. Dolomitization is observed only in one horizon, Plate 5.5A. The rhombs are well-developed and have a cloudy core (iron oxide) with iron oxide coating of the rims. Overgrowth is clearly observed in some of the rhombs, and the rims have sometimes corroded edges due to solution effects.

The dolomitization process had a destructive nature on the original depositional fabric. It created new fabrics and obscured all the original depositional fabrics. These fabrics implied that fluctuating oxidation-reduction potential in dolomitizing fluids prevailed through an open system of water circulation. This is exemplified in the alternation of ferroan dolomite and iron oxide zones in the dolomite rhombs.

5.5 Geochemical variation of some elements in conjunction with the dolomite distribution throughout the Pendleside Limestone Group

Geochemical analysis was carried out regarding the occurrence of elements such as magnesium, strontium, iron, and manganese in conjunction with the dolomite distribution throughout the Pendleside Limestone Group. These elements show a pattern of variation with the dolomitic horizons as will be discussed later. Concentration in parts per million for the previously mentioned elements were determined using the atomic absorption spectrophotometric method of analysis (Appendix B). Concentrations of magnesium, strontium, iron and manganese in the Hodder River section (100) are listed in Table 5.1. Concentration of the same elements in S. 400, S. 1200, S. 1300, S. 1500 and section PL+RW are listed in Tables 5.2, 5.3, 5.4, 5.5 and 5.6 respectively.

The concentration of each element in S. 100 in the Hodder River area, S. 400, S. 1200, S. 1300 and S. 1500 on Pendle Hill and the Salterforth section (PL+RW), were processed using the computer program (SYMAP). The resultant map shows the vertical and lateral variation of each element in the above mentioned sections and enables comparison with the distribution of dolomite established using the XRD data. The vertical and lateral map of the magnesium is shown in Fig. 5.17. On Pendle Hill (sections 400, 1200, 1300 and 1500) the magnesium shows an increase from the bottom of the map upwards. To the west and in section 100 the order is reversed, the increment being towards the lower parts of the succession. The same order is true for section PL+RW, the increment is towards the lower parts of the succession. If the magnesium map in Fig. 5.17 is compared with the dolomite distribution map (Fig. 5.16), there are some areas of high magnesium concentration which do not correspond to dolomitized zones. Examples of magnesium-rich undolomitized areas include the lower parts of S. 100 and section PL+RW (Fig. 5.17). Petrographic examination of thin sections revealed that the magnesium is concentrated in the microdolomite inclusions in grains such as echinoderm plates and crinoid stems which did not show up on the XRD analysis (Meyers and Lohmann, 1978).

The strontium concentration (Fig. 5.18) shows a relatively higher magnitude of Sr^+ concentration for the lower parts of sections 100 and PL+RW. This suggests a closed or restricted system and scarcity of solution percolating in these horizons (Kinsman, 1969). Whereas other areas that correspond to the dolomitized horizons show extremely low Sr^+ concentrations. This is due to the open-system of water circulation which removed some of the Sr^+ ions. This phenomenon is best explained by the mixing of fresh and sea waters, a mechanism proposed by Badiozamani (1973) for the hybrid type of dolomitization. Wherever the brackish water zone extended, dolomitization took place by consumption of Mg^{+2} ions available in sea water trapped in pore spaces. In contrast in the undolomitized

zones, Mg^{+2} ions are concentrated in inclusions found in echinoderm plates and crinoid stems. The strontium concentration values for the Hodder River section (100) are tabulated in Table 5.1; S. 400 (Table 5.2); S. 1200 (Table 5.3); S. 1300 (Table 5.4); S. 1500 (Table 5.5); and the Salterforth section (PL+RW) (Table 5.6). These values generally show extremely low concentration of Sr^+ compared with the Sr^+ concentrations in the present seas. Values above 1000 ppm are recorded from various localities in the present seas. Kinsman (1969) proposed a good interpretation for such low values of Sr^+ concentration in ancient carbonates. He stated that the Sr^+ concentrations of diagenetically altered limestones demonstrably to be of potential value in indicating the mechanisms of diagenesis. He suggested two simple diagenetic analogues, the closed system and the open system recrystallization of carbonate sediments in aqueous solutions. In the diagenetic alteration of typical carbonate sediments, the former process (closed system) may give rise to calcites with 700 - 10000 ppm Sr^+, whereas calcites with much lower Sr^+ concentrations may result from the later process (350 ppm or less). The low Sr^+ concentrations of the Pendleside Limestone Group dictate that an open system prevailed through which rather large volumes of pore fluids migrated during diagenesis. The Sr^+ concentration and prevalence of open system mechanism are in favour of the mixed water type of dolomitization mechanism thought to be responsible for the dolomitization of the Pendleside Limestone Group. The vertical and lateral variation of Sr^+ in Fig. 5.18 shows a pattern of distribution of the Sr^+ compared to the dolomitization map (Fig. 5.16). The Sr^+ values relatively increase where the dolomitization intensity decreases and show extremely low concentration in the upper parts of the map where the dolomitization is most intense.

The iron concentration in the map (Fig. 5.19) shows a predominence of iron in the Salterforth area (section PL+RW). This is due to the presence of thick beds of shale throughout the Pendleside Limestone Group in that area. Whereas on Pendle Hill and in

section 400, S. 1200, S. 1300 and S. 1500, the iron decreases and shows fluctuation in concentration in the upper parts of the succession due to the absence of shale beds. The increment is remarkable in the lower parts of the succession due to the presence of thick shale beds, compared with the upper parts of the succession of the Pendleside Limestone Group. This suggests that the iron concentration in the Pendleside Limestone Group is controlled by the presence of the thick shale beds at the bottom of the succession. This is confirmed by the petrographic examination of thin sections and field logging of the beds. The limestones at the lower parts of the succession adjacent to the shale beds show high content of iron oxide, ferroan calcites, and ferroan dolomites. In the upper part of the succession the carbonates are devoid of iron due to the absence of shale beds. This phenomenon was also observed by Oldershaw and Scoffin (1967) in their work on the Halkin and Wenlock limestones.

The manganese concentration values analysed by the atomic absorption (Tables 5.1, 5.2, 5.3, 5.4, 5.5 and 5.6) were also processed using computer program SYMAP. The resultant map (Fig. 5.20) shows the vertical and lateral distribution of manganese throughout the Pendleside Limestone Group. The manganese concentration shows a positive relation with the intensity of dolomitization when compared with the dolomite distribution map (Fig. 5.16). In the upper part of sections 400, 1200, 1300 and 1500 (Fig. 5.20), the manganese shows a relative increase in concentration compared with the lower part of the map. In section PL+RW the manganese concentration is relatively high only in the upper parts where the intensity of dolomitization is high, whereas in the lower parts the manganese concentration decreases. In the western parts of the map the manganese shows a relative increase compared with the eastern part of the manganese map. This is in conjunction with the relatively higher intensity of dolomitization in the western part of the map than in the eastern parts.

The results of the atomic absorption analysis in Tables 5.7, 5.8 and 5.9 were processed using computer program SYMAP. The vertical and lateral distribution of magnesium in Figure 5.22 suggests a periodicity in the concentration of magnesium throughout the Pendleside Limestone Group. The concentration increases at the top of the succession in the west and southwest and decreases at the top northeast corner of the map. If a comparison is made in between the dolomitization map (Fig. 5.21) and the magnesium distribution map (Fig. 5.22) high Mg^{+2} zones that are not dolomitized can be observed. These high concentration zones are located at the west and southwest corner of the map. The intensity of dolomitization wedges out in that direction (Fig. 5.21); although the magnesium concentration is as high as it is in the dolomitized parts of the map. This can be explained by the mixing waters type (brackish zone) of dolomitization (Badiozamani, 1973), where fresh water is mixed with sea water trapped in the pore spaces, thus forming brackish water zone in which dolomitization takes place.

The strontium concentrations are relatively low in value in the Slaidburn area. This suggests an open system (Kinsman, 1969) in which large volumes of pore fluids migrated during diagenesis. The strontium distribution map (Fig. 5.23) shows an increase to the south and southwest where the dolomitization is least intense, and conversely shows an increment above and below the wedging out of the dolomitization zone in Fig. 5.21.

The iron distribution map (Fig. 5.24) shows a general increase towards the west and southwest and a decrease towards the northeast. The distribution has congruency with the increment of the shale percent, which increases towards the basin and decreases away from the basin. This suggests that the iron is derived from the shale beds and its concentration follows the shale distribution.

The manganese distribution map (Fig. 5.25) shows a congruency with the dolomiti-zation (Fig. 5.21). The concentration of the manganese increases relatively with the dolomitization increase in Figure 5.21, and decreases away from it. The manganese concentration shows a remarkable decrease in the west and southwest (towards the basin) and an increase towards the northeast especially towards the dolomitization zone.

5.6   Relationships between porosity and dolomitization

Many authors have discussed porosity and its relation to dolomitization, especially when porosity becomes potential oil reservoirs in many dolomitized oil bearing formations. Lands (1946) discussed porosity through dolomitization; his work is based on the Trenton oil field of Ohio, Indiana, and the Adams and Deep River oil fields in Michigan. Weyl (1960) demonstrated and calculated the requirements for the conservation of mass of the chemical constituents of the rock and the interstitial solutions and placed limits on the process of porosity formation. Murray (1960) discussed the origin of porosity in carbonate rocks, and he referred especially to the porosity type produced by sucrose dolomite.

Evidence indicates upon the petrographic examination of some dolostones and dolomitic limestones in the Pendleside Limestone Group, that porosity is formed by the growth of randomly oriented, uniformly sized dolomite euhedra, accompanied or followed by dissolution of non-replaced calcites (Plate 5.5B and C). Petrographic evidence for the origin of porosity in the dolomitized zones comes from areas where all degrees of dolomitization are present in intimate vertical and horizontal association. The highly dolomitized limestones generally are concentrated in the upper parts of the Pendleside Limestone Group. In addition the original limestone shows all gradations from sorted carbonate sands to muds with varying amounts of contained carbonate sand-sized particles. The sand size particles include crinoid parts, echinoderm plates, peloids and ooids. In

the slightly dolomitized limestones, the dolomites occur as scattered perfect rhombs. These rhombs are of replacement origin and appear to occupy volumes once occupied by parts of peloids (Plate 5.6A), fossil fragments (Plate 5.6B), fine carbonate muds. As the dolomite content increases, the number of rhombs increases. In general the rhombs in an individual sample are relatively all the same size and appear to show little, if any, preferred orientation. At an average of 50 per cent dolomites, the dolomitization has obscured most of the original very fine calcite mud and particles, leaving only small patches of the original texture and faint ghosts of particles.

Murray (1960) plotted the porosity versus dolomite content and indicated that there is a slight decrease in porosity up to approximately 50 per cent dolomite, but as the dolomite content increases above 50 percent, the porosity rapidly increases to higher values. He deduced from his observations that porosity and pore size increases as complete dolomitization is approached. In regard to the carbonate ions, as suggested by Murray (1960) there are two possible assumptions:-

i) Carbonate ions that are brought to the site of the rhomb growth in solution from other rocks (distant source).

ii) Carbonate ions derived locally from the rock being dolomitized during dolomitization (local source). If the new dolomite crystals are grown from solutions that are bringing carbonate into the rock being dolomitized from a distant source, the porosity should decrease. If the porosity of the volume being replaced by one dolomite crystal is less than approximately 43 per cent, there will be sufficient calcium to combine with the magnesium to produce the dolomite. The increase in porosity above 50 per cent dolomite, with increasing dolomite content, but similar dolomite rhomb size and texture, indicates that the original calcite matrix between the dolomite rhombs has been dissolved to produce void space.

Murray (1960) recognized dissolution of calcite from a dolomitic limestone as the origin of dolomite porosity, but he considered selective leaching at an unconformity by meteoric waters as the mechanism. Dissolution of the calcite in the Pendleside Limestone Group could have taken place during and contemporaneous with the dolomitization process. According to Weyl (1960) an assumption can be made that the carbonate mud with abundant sand size carbonate particles had approximately 21 per cent porosity at the time of dolomitization. The growth of a dolomite rhomb would involve the consumption of magnesium found in the system, and the dissolution of some calcite near the site of the rhomb could provide the necessary carbonate for filling the pore spaces within the volume of rhomb growth plus the 12 - 13 per cent porosity difference occasioned by growth of the denser mineral dolomite. Excess calcium ions must be removed from the system. If the dolomitization process is carried to completion all the calcite will be used to form dolomite. The resulting rock would have a porosity, assuming no compaction during and following dolomitization, equal to the sum of the original porosity plus an increase of 12 - 13 per cent of the calcite originally present.

Further study of the porosity through dolomitization has been established by scanning electron microscopy. The scanning electron microscope has been used and proved to be an effective tool in the study of porosity through dolomitization. The electron micrographs obtained show the presence of porosity zones around and within the dolomite crystals. These are believed to be the result of the dissolution of calcite at random points, so providing the necessary carbonate and calcium ions for the growth of the dolomite rhombs. The natural fractured surfaces of selected dolomitized rocks were prepared for examination by the scanning electron microscope. These surfaces are not etched by acid, because such a treatment would interfere with the natural texture and eventually cause misinterpretation, such as with Gillot (1969). Polishing was also avoided,

since some dolomite and calcite crystals tend to be destroyed or pulled out in the process. The surfaces of the specimens are coated with carbon for the purpose of conductivity.

In the dolomitized rock a clear textural relationship between calcite and dolomite, and between the dolomite and the surrounding matrix was observed during the scanning electron microscope examination of the samples. Dolomite occurs in a euhedral shape, separated from the calcite by irregular voids or pores which vary in size and extend into the calcite grains. The dolomite relationship in the carbonate rock is clearly shown in Plate 5.7A and B, in which a euhedral dolomite rhomb in a calcite matrix is surrounded either partly or almost completely by an irregular porosity zone. The pores are not confined to the area immediately around the rhomb but seem to extend to some short distance from the rhomb. The dolomite rhomb appears to be attached to the matrix at one side irregularly by a relict link extending across the porosity zone (Plate 5.7A). The examination of the samples in this work has revealed significant evidence supporting the hypothesis of dolomitization from locally derived carbonate ions. In Plate 5.7D (from the Hodder River area) the electron micrographs show clearly the dissolution of calcite and the construction of honeycomb texture (Gillot, 1969; Al-Hashimi, 1970). The electron micrographs show scattered rhombohedral crystals of dolomite of various sizes within the limestone matrix (Plate 5.8A). These rhombs are often surrounded by a high porosity zone, either in the form of honeycomb texture, or in the form of a simple dolomite crystal. Examination of various other dolomitized rocks has disclosed that they show similar features regarding the porosity zone around the dolomite rhombohedra (Plate 5.8B).

Bubb and Perry (1968) have shown by laboratory experiment that the concept of dolomitization using a local source of carbonate ions is valid, and the resultant porosity is not in the form of uniformly distributed pores surrounding the growing dolomite crystals. They emphasized that the transfer of carbonate ions does not necessarily need to be from

calcite adjacent to the growing dolomite, but may come from other established areas of

dissolution. This seems to explain the presence of pore concentration in the calcite matrix

present, such as in Plates 5.7C and 5.8C. The calcite matrix seems to dissolve in order

to provide the carbonate ions necessary for the dolomite crystal growth. The degree of

preservation or destruction of these resultant pores depends on the dolomitization which

took place as early as the first generation cement and created these pores. The effect

of compaction decreased when the dolomite started to form a supporting framework at

about 50 per cent dolomitization (Murray, 1960), thus preserving the pore spaces. During

the SEM examination of dolomitic limestone, some voids are found within single dolomite

crystals (Plate 5.8B). These do not seem to have formed during the fracturing of the

rhomb, since the surface texture of each dolomite crystal is flat and lacks projections.

Thus two possibilities can account for the formation of such pores: either these pores

arose as a direct product of the later dolomite replacement of the calcite cores with a

local source providing the carbonate ions, or they resulted from a later solution of calcite

relics remaining in the dolomite crystals. The later possibility is more likely to have

happened. If these voids resulted from a later dolomitization process, only the outer part

of the crystal would have been affected. The fracture in Plate 5.8B indicates that the

voids extend to the core of the crystal and are uniformly distributed throughout the dolomite

crystal. Al-Hashimi (1970) agreed with Gillot (1969) about the skeleton of the honey-

comb texture which is composed of clay minerals and other insoluble material, originally

present at the boundaries of calcite grains, and entirely unmodified from their original

distribution.

However, evidence obtained from the present work suggests that this texture resulted

from the continuing dissolution of calcite crystals which provided a local source of

carbonate ions for the growth of dolomite crystals. As a result of this dissolution a

skeleton of the acid insoluble material was left behind forming the honeycomb texture.

Such a texture would probably be only a single, irregular porosity zone surrounding each

dolomite crystal (Plate 5.8A and B). The origin of the honeycomb texture and single

porosity zone is found to agree with the hypothesis proposed by Murray (1964) based on

a conventional microscopic investigation into the origin of clear-rimmed and cloudy-

centered dolomite crystals (Plate 5.6C). He suggested:-

1.   Dolomite begins growth by replacement. The excess carbonate needed

      for the growth of the rhomb is supplied by dissolution of calcite beyond

      the limits of the rhomb.

2.   Excess dissolution of calcite beyond the limits of the rhomb creates higher

      porosity immediately around the growing crystal.

3.   Continued removal of calcite produces a very high porosity zone around

      the growing crystal. The inclusion-free rim begins to form because of

      lack of calcite available for inclusion.

4.   The very high porosity zone continues to expand with continued crystal

      growth producing an early stage cloudy centre with a late stage clear rim.

      Compaction of the unreplaced limestone could destroy the high porosity

      zones remaining around the crystal when growth ceases.

The petrographical study of some dolomitized limestones shows that most dolomite

crystals have clear rim and a cloudy centre. The cloudy centre results from dolomite

replacement of calcite allochems, e.g. peloids, (Plate 5.3A and C) and the clear rim

results from calcite dissolution immediately around the dolomite crystal to provide the

excess carbonate ions necessary for the growth of the crystal. Usually the dolomite starts

to form an overgrowth on the calcite elements (syntaxial growth) and then replaces them.

Overgrowth of clear dolomite is often found on peloids. These peloids are usually very

resistant to dolomitization and in most cases they remain unreplaced and form a calcite core within the dolomite crystals. During progressive dolomitization this core will finally be replaced by the dolomite and a ghost of the former fragment, e.g. peloid will be left as a cloudy centre.

5.7   Compositional zonation of some dolomite rhombohedra

Numerous occurrences of zoned dolomite crystals have been cited in the literature (Cayeux, 1935; Shearman et al., 1961; Evamy, 1963; Delinger, 1964; Murray, 1964; Friedman and Sanders, 1967; and Katz, 1968 , 1971).

During the microprobe scan (Appendix D) of some dolomite rhombs, compositional zonation of dolomite rhombs was observed. These dolomite rhombs contain geometrically well-defined rhombohedral cores and/or zones (Plates 5.3B, 5.5C, and 5.6C). Traverses across the rhombs revealed compositionally variable Ca:Mg:Fe ratios within the rhomb, but generally all the rhombs proved to be calcian in composition.

In the Rad Brook section (RB) (788428) on Pendle Hill (sample RB44), the structural formula shows variation in the calcium:magnesium ratio in the range of $Ca_{0.62-0.64}$: $Mg_{0.42-0.47}$ (Fig. 5.26A). The core of the rhomb shows an increase in the magnesium ratio compared to the outer zone of the rhomb. In another scan for a different rhomb in sample RB44, the calcium:magnesium ratio varied as a traverse is made across the rhomb (Fig. 5.26B). In this rhomb, the B zone, which is very narrow, shows a low Ca:Mg ratio relative to the core and the outer zone A. This is probably due to the interface in between the original boundary of the dolomite rhomb and the subsequent overgrowth.

In sample RB46 from the top of section Rad Brook (788428) on Pendle Hill, two traverses were made across two different rhombs (Fig. 5.27A and B). In the first traverse

(Fig. 5.27A) the rhombs have a high magnesium:calcium ratio in the core as the structural

formula in zone B indicates. The Ca:Mg ratio increases towards the outer zone of the

rhomb. The iron content in the core is high, and decreases towards the outer zone, of

the dolomite rhomb.   In sample RB46 (Fig. 5.27B), traversing across

the rhomb revealed a non/ferroan dolomite core and the iron content is extremely low , but

reappears towards the fringes of the rhomb and reappears at the rim. The magnesium

shows an inverse relation with the iron content. This is well demonstrated in the ferroan

dolomite structural formula in Figure 5.27B.

Upon the scanning of sample 1220 from section 1200 (779415) on Pendle Hill, two

types of rhombs are encountered. The first type (Fig. 5.28A) is a dolomite rhomb with a

haematite core, with the amount of iron decreasing in the successive zone and reappearing

again at the rim. The structural formula in zone B shows the decrease in Ca:Mg ratio

similar to the previously described samples (RB44 and RB46) from the Rad Brook section. In

the second type (Fig. 5.28B), the dolomite rhomb does not show a haematite core as

revealed by the structural formula at zone C. The core of the rhomb is mainly calcian

dolomite with 3:2 ratio of Ca:Mg. The proportion of the Ca:Mg ratio varies away from

the core. The rims of the rhomb show a high content of haematite. The B zone shows a

low content of Ca:Mg as in previous rhombs.

Upon the gathering of the data obtained by the microprobe traverses of the dolomite

rhombs and in conjunction with the petrographic examination of the thin sections, two

types of dolomite rhombs are encountered.

i) Dolomite rhombs with haematite core, and a clear rim (Plate 5.6C, Fig. 5.26A,

5.27A and B and 5.28A & B.

ii) Dolomite rhombs with a haematite-free core and haematite rim (Plate 5.3B,

Fig. 5.27B and 5.28B).

The texture and zonation of the calcian and ferroan dolomites and their crystal-lographic orientation show that they represent growth stages of the dolomite crystals. Thus, they should reflect compositional changes of the interstitial solution with respect to their dissolved Ca^{+2}, Mg^{+2} and Fe^{+2} contents during dolomite crystal growth.

Katz (1971) referred the ferroan dolomite formation to the replacement of Fe^{+2} ions to the Mg^{+2} lattice sites. The Fe^{+2}:Mg^{+2} ratio increase in the solution and the formation of ferroan dolomite is brought about. The increase in the Fe^{+2}:Mg^{+2} ratio can not be attributed to significant decrease of the magnesium ion activity because this would prevent the formation of dolomite. The increase of the Fe^{+2}:Mg^{+2} ratio should, therefore, be mainly related to an absolute increase of ferrous iron activity in the solution which, in turn, depends mainly on the pH and Eh of the system, increasing to these parameters.

Katz (1971) assigned the existence of the haematite zones and cores as products of oxidation of ferroan dolomite zones and cores. In the Pendleside Limestone Group oxidation took place during periods of fresh water impulses from land areas as suggested by the mechanism of mixing fresh and trapped sea waters in the brackish water zone. The following observations are relevant in the explanation of the haematite zone mineralization:-

1. The textures of the ferroan dolomite and of haematite zones are identical, since the former is interpreted as a crystal growth product, the latter should best be considered as a pseudomorphic feature.

2. Inner cores and zones of haematite are followed by outward fresh, unoxidized zones of ferroan dolomite (Plate 5.5C). If oxidation occurred after completion of crystal growth only the exterior ferroan dolomite should have been affected by it. This suggests two episodes of oxidation and thus,

two episodes of fresh water influx to the site of dolomitization.

3. Haematite mineralization extends from the haematite zones inwards, but

    not in the opposite direction (Plates 5.3B, 5.4B and C).

4. Fresh, unoxidized ferroan dolomites zones are widespread in the Pendleside

    Limestone Group (Plates 5.3C and 5.4A). These show no haematite

    enrichment on the rims of the rhombs.

Alternatively, it can be suggested that haematite zones are formed by periodic

precipitation of ferric hydroxide, directly from interstitial solutions upon the growing of

the dolomite crystals. Such a mechanism, however, is unlikely in the light of the

following considerations:-

a) Rhombohedral haematite cores are clearly produced by a pseudomorphic

    process and could not have formed by direct precipitation.

b) Relict patches of dolomite always occur within haematite zones and cores

    and have the same orientation as the host crystal (Plate 5.5C). How could

    these patches occur or be supported, if haematite precipitated directly

    from solution?

c) The corrosive texture displayed by dolomites in contact with haematite

    zones is indicative of a pH decrease of the solution in contact with it.

    This decrease can easily be ascribed to the oxidation of ferrous carbonate

    to haematite during which hydrogen ions are released into the solution.

    A precipitate of ferric hydroxide settling upon the dolomite crystal surface

    might perhaps protect the crystal from chemical activity of the solution,

    but can not explain the corrosion of the dolomite.

5.8 Structural and compositional variation of some dolomites

Graf and Goldsmith (1956) and Goldsmith and Graf (1958) observed that synthetic dolomites formed under a variety of experimental conditions go through a protodolomite stage of development. These protodolomites contained more than 50 mole percent $CaCO_3$ in the structure and the X-ray diffraction graphs show weak or even absent order reflections, as well as basal reflections that are broadened or diffuse to those reflections with little or no c-axis contributions. These imperfectly crystallized materials, if held long enough at an adequately high temperature, approached ideal dolomite both compositionally and structurally. A similar method for examining some powdered dolomite samples was carried out to detect the degree of ordering and the development of the set of planes parallel and/or perpendicular to the c-axis. The examination of the powdered dolomites is carried out using routine X-ray diffraction methods.

An ideal dolomite is defined as one with 1:1 molar $CaCO_3$:$MgCO_3$ ratio that gives an X-ray diffraction pattern containing the complete set of reflections of proper relative intensity characteristic of the dolomite structure. Most sedimentary dolomites that are low in Fe^{+2} and Mn^{+2} appear to approach this definition fairly closely although they often appear to be rich in calcium.

Goldsmith and Graf (1958) gave detailed chemical analyses and unit-cell size determination on five coarsely crystalline dolomites free of extraneous phases. Even among these well-crystallized dolomites, it can be noted that in the sensitive back reflection region some of the dolomites show an observable diffuseness of those reflections that have a strong c-axis component, whereas reflections that have a strong a-axis component are quite sharp. This feature, although not striking, is characteristic of many dolomites in the Pendleside Limestone Group, and indeed is observed in a variety of

multi-cation rhombohedral carbonates, both ordered and disordered.

Goldsmith and Graf (1958) gave three aspects for the variation of natural dolomites from the essentially ideal dolomites:-

1. They have an enlarged unit cell that can be shown to be due to the presence of $CaCO_3$ in the structure in excess of 1:1 molar $CaCO_3:MgCO_3$ ratio. This is true in the Pendleside Limestone Group since some of the dolomites tend to be more calcian than approaching the ideal dolomite of 1:1 ratio of $CaCO_3:MgCO_3$.

2. The reflections with a strong c-axis component are characteristically more diffuse than those with strong a-axis components. This effect is markedly greater than that observed for the essentially ideal dolomites and in some cases it can be observed even in the front-reflection region. The intensity distribution of the reflections from planes normal or nearly normal to the c-axis is generally asymmetrical, tailing-off towards larger 2θ-values. In some cases the distribution may even be bimodal.

3. The principal order reflections characteristic of the dolomite structure (Bradley, Burst and Graf, 1953; Graf and Goldsmith, 1956) appear in many cases to be somewhat weakened relative to those reflections common to both calcite and dolomite structures. This is an expected consequence of a deviation from the ideal dolomite composition and of any other structural deviation from the ideal ordered cation sequence.

These three effects, which are, in principle, the same as those observed in the synthetic protodolomites, are not independent, but occur together. X-ray patterns of some samples of ordered and disordered Ca-rich dolomites are represented in Fig. 5.29.

The complete set of samples are described in Table 5.10. The portions of diffractometer patterns (Fig. 5.29) were obtained using Ni-filtered CuKα_1 radiation. The upper portion of the pattern (Fig. 5.29A) shows a disordered Ca-rich dolomite with no reflection from the set of planes parallel or perpendicular to the c-axis. In Figure 5.29B the pattern shows a slight reflection from the set of planes parallel to the c axis whereas it shows no reflection at 35° 2θ which means it is a disordered dolomite. Ordering reflection is slightly moderate in Fig. 5.29C where an attenuated reflection from the 01.5 indices 35° 2θ is observed. Moderate reflections are also observed from the set of planes parallel and perpendicular to the c-axis (11.0 and 00.6 respectively). An ordered reflection can be seen in Figure 5.29D where a good reflection at 35° 2θ (01.5) indices and good reflection can be observed at 37° 2θ (11.0) and 33° 2θ (00.6) set of planes parallel and perpendicular to the c-axis respectively. The later reflections mean that well-developed crystal planes are present in the ordered dolomite crystals.

According to the data in Table 5.10, the dolomites in section 1500 (761393) on Pendle Hill show generally a good ordering reflection and a well-developed crystal plane parallel and perpendicular to the c-axis as can be indicated by the pattern of reflection indices (11.0 and 00.6 respectively). The dolomite shows an increase in ordering towards the upper parts of the succession, though there are a couple of exceptions. In section 500 (787426) on Pendle Hill, the dolomites are well-ordered according to their reflection pattern and the set of planes parallel and perpendicular to the c-axis are well-developed as can be indicated by the reflections of 11.0 and 00.6 indices respectively. In the Slaidburn area, section 300 (718501), the dolomites show a complete disordering and the reflections from the set of planes parallel and perpendicular to the c-axis are completely absent and diffused.

Goldsmith and Graf (1958) referred the disordering of the dolomites to the presence of multi-cation rhombohedral carbonates such as iron and manganese which replace the magnesium in the structure of the dolomite, thus defecting and increasing the unit cell size of the dolomite structure, or the presence of excess $CaCO_3$ in the dolomite (which is certainly the case in the dolomites of the Pendleside Limestone Group as revealed and proved by microprobe analysis of the dolomite samples). The last reason proposed by Goldsmith and Graf (1958) is that the disordering of the dolomites is due to the presence of intimate intergrowths of rhombs that have similar values for the a-axis indices, but different values for the c-axis indices, thus increasing the degree of disordering in the dolomite. This is observed in section 1500 (761393) by the petrographic examination of some thin sections which show intergrowths of rhombs (Plate 5.5C).

5.9 Dedolomitization in the Pendleside Limestone Group

Dedolomitization is the replacement of dolomite by calcite in carbonate rocks (AGI , Glossary of Geology, 1972). This process is now widely rocognized in the stratigraphic column. Dedolomitization was first proposed by Von Marlot (1848); later it was used by Teal (1903) and Faust (1949) to describe the breakdown of dolomite at high temperatures under metamorphic conditions. Dedolomitization has been reviewed briefly by Friedman and Sanders (1967) and recent work on dedolomitization has been carried out by Shearman et al. (1961), Evamy (1963, 1967), Swett (1965), Schmidt (1965), De Groot (1967), Katz (1968, 1971), Al-Hashimi and Hemmingway (1974), Al-Hashimi (1972), Braun and Friedman (1970), Moor (1971) and Zenger (1973).

In these works the understanding of this process may shed light on the diagenetic

history of the carbonate rocks. As suggested by Braun and Friedman (1970) and agreed by many authors indicators of surface weathering such as dedolomitization can be very useful in locating unconformities, or possibly leading to the location of sucrose dolomite which are potential reservoirs for fluids, hydrocarbons and water (Evamy, 1967).

Dedolomitization is effectively brought about by solutions with a high Ca:Mg ratio reacting with dolomite to form calcium carbonate (dedolomite). The reaction is presented by the equation originally proposed by Von Marlot in 1848:

$$CaCO_3.MgCO_3 + Ca^{++} \xrightleftharpoons[\text{dolomitization}]{\text{dedolomitization}} 2\,CaCO_3 + Mg^{++}$$
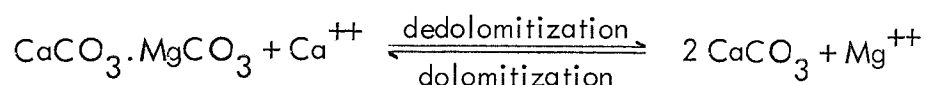
In this reaction sulphate ions should be available to promote its continuity. These should be derived either from the solution of gypsum or anhydrite (Von Marlot, 1848; Shearman et al., 1961) or from the oxidation of pyrite (Evamy, 1969) Zenger, 1973). Most of the aforementioned authors considered that dedolomitization is of late diagenetic or epigenetic stage. Katz (1968) considered that dedolomitization is an early diagenetic process related to the physio-chemical changes in the overlying and interstitial water system. This process is therefore independent of near surface conditions. The following features served as criteria of disinguishing dedolomites during the petrographic investigation:

A)   The presence of composite or polycrystalline calcite rhombohedra (Plates 5.8D, 5.9A and B) that were stained with Alizarin Red S and potassium ferricyanide (Appendix A). Calcite and dedolomite stained mauve-pink (Plate 5.10A and B).

B)   The presence of rhombohedral outlines stained with iron oxide, or in some cases the development of patches of iron oxide. The iron oxide in the dedolomites was produced after the completion of the crystal growth. The

following observations are made:-

1. In the dedolomites, iron oxide is distributed across the margin of the rhomb pseudomorphs and this penetrates both calcite rhombs and part of the adjacent matrix (Plate 5.10B). It would therefore appear that alteration took place after completion of crystal growth.

2. It is also observed that in most of the dedolomites only the outer-most zone (rim) has been oxidized.

3. Oxidized and unoxidized parts in the same zone can not be assumed to have been formed during crystal growth. If this was true, then the zone would have been completely oxidized.

4. The presence of completely oxidized rhombohedra is clear evidence of oxidation after growth.

5. Some of the dedolomite rhombs show a deformed texture such as broken rims that are replaced or intruded by silica. This suggests that the dolomite rhombs originated before the silicification took place. If these rhombs were dolomite rhombs during and after silicification and then dedolomitized, they would not develop such pores that are replaced and/or intruded by silica. A texture and pore system such as that described is likely to develop during dedolomitization.

6. The occurrence of iron oxide around the rim and along fissures can be explained by the expulsion theory. The expulsion of foreign material during crystal growth is likely to happen. This is observed where a concentration of undigested materials are found along the margin of dedolomite rhombs. Thus the presence of iron oxide can be explained as physical displacement of iron which has difficulty to fit in the lattice requirement during the growth of secondary calcite.

Evamy (1963) suggested that sulphate ions are liberated during the oxidation of pyrite in the limestone. These sulphate ions are potential agents for the dedolomitization process:

$$CaSO_4 + MgCO_3 \cdot CaCO_3 \rightleftharpoons 2\,CaCO_3 + MgSO_4$$
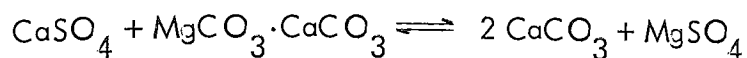
This is unlikely in the Pendleside Limestone due to the following:

1. If this mechanism was responsible for the dedolomitization in the Pendleside Limestone Group there should have been a major dedolomitization throughout the dolomite due to the presence of pyritic material throughout the Pendleside Limestone Group. Only one horizon has been found dedolomitized throughout the Pendleside Limestone Group.

2. No $MgSO_4$ has been found in the thin sections nor during the X-ray diffraction of the samples.

3. No indication of $CaSO_4$ has been observed or examined in the thin sections nor during the X-ray diffraction of samples.

Al-Hashimi (1973) proposed a mechanism whereby ferroan dolomites, which are compositionally metastable, gradually become altered or replaced by calcite. This metastability may be either caused by some disordering in Fe^{+2} cations, or by the presence of more than 50% $CaCO_3$ in the ferroan dolomites. These dolomites may become increasingly metastable under surface conditions. In this connection Berner (1971) stated that iron carbonates are thermodynamically unstable in sea water and may suffer alteration. Yanat'eva (1955) demonstrated that dolomite dissolves incongruently

under surface conditions. If this is valid, then the general form of ferroan dolomite

breakdown as proposed by Al-Hashimi (1973) will be:-

$$4CaMgFe(CO_3)_2 + 2H_2O + 2O_2 \longrightarrow 4CaCO_3 + 2Fe_2O_3 + 4Mg^{+2}$$
$$+ 2CO_3^{-2} + 2H_2CO_3$$
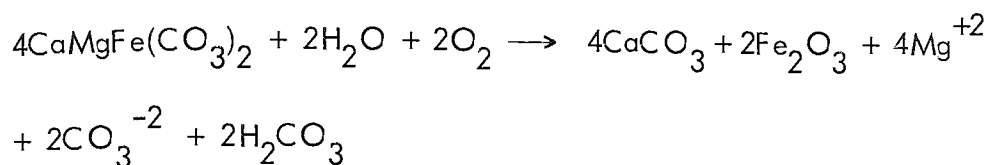
The aforementioned reaction is very likely to have happened in the Pendleside

Limestone Group. X-ray diffraction has revealed that the ferroan dolomites are calcian

in composition and lithological evidences, e.g. formation of peloidal limestones suggests

nearness to surface conditions whereby dedolomitization took place in the Pendleside

Limestone Group.

5.10 Proposed mechanism responsible for the dolomitization
of the Pendleside Limestone Group

5.10.1 Introduction

The genesis of dolomites and the process responsible for dolomitization have

attracted the attention of scientists for many years. The observation of the paucity of

recent dolomites in comparison with the massive volume of older dolomites, and the

failure to produce this mineral experimentally at near-surface temperature and pressure

initiated the so-called "dolomite problem". The complexity of the problem is enhanced

by kinetic factors that apparently inhibit dolomite precipitation from sea water. Dolomite

does not precipitate from sea water although the water is many times supersaturated with

respect to the mineral. Also, dolomitization of carbonate sediments in direct contact

with sea water is rare (Sonnenfeld, 1964). Although the mechanisms and physico-

chemical conditions suitable for dolomitization are still ambiguous and not fully understood,

knowledge of the environment of deposition can result in distinction between primary and secondary dolostones. Discovery of recent dolostones in Southern Australia (Alderman and Skinner, 1957); Andros Island (Shinn et al., 1965), Persian Gulf (Illing et al., 1965) and other localities provided valuable information regarding the environment of deposition of the dolomite; results of these studies were applied to the geologic record. Using the present as a key to the past a close association of recent dolomites with evaporite minerals led to overgeneralizations, such as "most dolostone deposits in the geologic record owe their origin to hypersaline brines. They must therefore be considered as evaporite deposits". (Friedman and Sanders, 1967)

Widespread dolomitic facies associated with shallow epicontinental shelves or structural highs (Badiozamani, 1973) constitute substantial amounts of dolostones that are devoid of evaporites and lack evidence of supratidal origin. Hypersaline dolomitization models, therefore, fail to propose a suitable mechanism of dolomitization for these sediments. A dolomitization model that is independent of evaporation or high Mg^{+2}/Ca^{+2} ratio in solution is required in order to provide a good explanation of the genesis of dolomites associated with continental shelves or positive elements (Badiozamani, 1973).

Extensive studies regarding the mechanisms of dolomitization in recent environments have been carried out in the past decade. A summary of classification of dolomitization mechanisms is given in Fig. 5.30. Although dolostones have a variety of origins it is likely that the majority have a secondary origin according to the literature (Garrels and Mackenzie, 1971; Badiozamani, 1973). Only a small fraction of the dolostones which are associated with evaporites are considered to be primary. Secondary dolomitization may occur during early stages of diagenesis, i.e. penecontamporaneous dolomitization, or it may occur later in the history of the rock. A condition of all the models proposed, except for the Dorag and Cannibalization models (Fig. 5.30) is that the solution should

be many times supersaturated with respect to calcite and dolomite. Also, common and necessary requirements of all the models for dolomitization are an almost unlimited source of Mg^{+2} and a mechanism for circulation of reactive fluids through the pore spaces. Circulation is required to supply the mass of Mg^{+2} necessary for the dolomitization reaction. Mechanisms currently favoured for obtaining circulation are evaporation (Sabkha model, Illing et al., 1965); density gradients (Bonaire model, Deffeyes et al., 1965); and hydrostatic head models (ground water model, Hanshaw et al., 1971); and the cannibalization model (Goodell and Garman, 1969). The mixed water type (Dorag) model can be shown to be most applicable to the Pendleside Limestone Group.

5.10.2 Dolomitization by ground water mechanism

Hanshaw et al. (1969, 1971) proposed dolomitization by ground water with some modification to account for the amount of Mg^{+2} necessary for massive dolomitization. In their modified model, dolomitization is postulated to occur in the brackish water zone that results from mixing of fresh and sea water (Badiozamani, 1973). In this zone, Mg^{+2} ions are supplied by sea water, and dissolution of $CaCO_3$ occurs owing to the mixing of the two waters. Lands (1972) and Durham and Olson (1978), also employed the same mechanism of dolomitization for the dolomites in the Jamaican reef, and the Cordilleran formation in Nevada.

The study of palaeontology, stratigraphy and facies distribution in conjunction with the petrographic analysis, provided information necessary to the interpretation of the variation and relative depth of the depositional environment as well as the vertical and horizontal configuration of the dolostone-limestone horizons. The following observations were made during the analysis of samples from the Pendleside Limestone Group:-

1. During the petrographic examination of some thin sections, it is observed that dolomite horizons are preceeded and succeeded by the occurrence of undolomitized peloidal or oolitic limestones. This phenomenon is observed in many horizons in the Hodder River section (100) (702339), Rad Brook (RB) (788428) and section 200 (723503) in the Slaidburn area (Plates 5.10C, 5.11A, B and C). The peloidal limestones represent periods of maximum limestone deposition prior to subsidence during which fresh water from land areas in the south and probably north propagated and mixed with trapped sea water in the brackish water zone, thus dolomitizing the limestones (Badiozamani, 1973; Durham and Olson,1978).

2. The spatial distribution of the dolomite horizons vertically and laterally in the Pendleside Limestone Group suggests that different episodes of dolomitization took place during periods of maximum limestone deposition prior to subsidence. This means that dolomitization is of an early diagenetic origin. If the dolomitization was of a late diagenetic origin (after the deposition of the Pendleside Limestone Group was completed), the peloidal limestones in between dolomite horizons would not remain undolomitized.

3. The textural variation of dolomite rhombs are in favour of different diagenetic episodes of dolomitization. In the lower parts of the Pendleside Limestone Group, the dolomite horizons have distinct rhombs of ferroan dolomites, whereas in the upper parts the whole rock has been dolomitized and the rhombs do not resemble the lower part dolomite rhombs and are devoid of ferrous iron.

4. In recent carbonates Na^+ concentrations have been reported to be around 1500 - 1800 ppm (Badiozamani, 1973; Harris and Pikely, 1966). The mean value of Na^+ concentration in the Pendleside Limestone Group is 800 ppm, and for the dolomite

facies is 200 ppm. These Na^+ values of the Pendleside Limestone therefore strongly suggest the equilibrium of these carbonates with meteoric water and the loss of Na^+ through diagenetic processes.

5.   Analysis regarding the Sr^+ ion concentration shows extremely low values (350 ppm) for the Sr^+, in the limestones (Tables 5.1 - 5.9). Such low Sr^+ concentrations of the limestone dictate that an open system prevailed through which rather large volumes of pore fluid migrated during diagenesis (Kinsman, 1969).

6.   The physio-chemical properties of dolomite crystals formed from slow growth are relatively large, well-ordered dolomite crystals, containing low concentrations of foreign ions (Goldsmith and Graf, 1956). By contrast, rapid crystallization produces very small, poorly ordered dolomite crystals, containing high concentrations of foreign ions (Land et al., 1975). Both types of dolomite rhombohedra exist in different horizons in the Pendleside Limestone Group. If the dolomitization was of a late diagenetic origin and of only one episode then only one type of dolomite rhomb would have existed: either well crystallized ordered dolomite, or poorly crystallized disordered dolomite.

7.   The lack of occurrence of evaporites in association with the dolomites favours the mixing type of dolomitization.

Gathering the evidence listed above, the replacement dolomite in the Pendleside Limestone Group is formed in response to the dilution of marine pore water by fresh water in the brackish water zone (Fig. 5.31). Intrusion of fresh water into the marine-deposited sediments took place as a result of lateral extension of fresh water lenses that had developed and extended from the south and southwest parts of the Craven Basin probably from the Derbyshire massive and Widmerpool Gulf towards the north and

northwestern parts of the basin. In the Slaidburn area dolomitization took place as a result of intrusion of fresh water lenses that penetrated the area from the north probably from the Askrigg Block area which have been a positive area during periods of maximum limestone deposition prior to subsidence.

In general the extension of fresh water commenced during periods of maximum limestone deposition and prior to subsidence of the sea floor (Fig.5.31). Pervasive dolomitization of the original $CaCO_3$ sediments was the result of this process.

5.11   Discussion and conclusions

One of the important diagenetic processes and most influential one in the Pendleside Limestone Group is dolomitization. This process involved many separate limestone horizons in the Pendleside Limestone Group, some of which (uppermost part) are completely dolomitized. The mechanism thought to be responsible for the dolomitization is the mixing of fresh and sea waters in the brackish water zone. The source for magnesium ions is the high magnesian calcites deposited originally from sea water. This is indicated by the microdolomite inclusions found in echinoderm plates and crinoid stems (Meyers and Lohmann, 1977). Trapped sea water in pore spaces also provided magnesium ions necessary for the dolomitization process. The source for carbonate ions is the local dissolution of calcite and formation of cavities and vugs forming a honeycomb texture in some of the limestones (Gillot, 1969; Al-Hashimi, 1970). This is indicated by the photomicrographs of the scanning electron microscope (Plate 5.7C and D).

The following are relevant regarding the mechanism and the diagenetic stage of formation of dolomites:-

1.   The textural relationship of dolomite rhombs with the allochemical constituents,

e.g. ooids and peloids, suggests an early origin of the diagenesis of the lime-
stones regarding dolomitization.

2. The low Sr^+ concentration in the limestones suggests an open system (Kinsman,
1969) during which a large volume of fluids carried away the Sr^+ ions from the
environment of deposition.

3. The Na^+ concentration also suggests the loss of this ion due to the diagenetic
influences such as percolation of fluids in an open system, thus decreasing the
Na^+ concentration in the Pendleside Limestone Group.

4. The spatial distribution of the dolomite horizons in the Pendleside Limestone
Group suggests separate episodes of dolomitization. This is indirectly related
to the early diagenesis of each dolomitized limestone horizon in the Pendleside
Limestone succession.

5. The physio-chemical properties of dolomite crystals formed in the upper part
of the Pendleside Limestone suggests that the rhombs are formed from slow
growth. The relatively large, well-ordered crystals of the dolomite containing
low concentration of foreign ions (Goldsmith and Graf, 1958) at the upper parts
of the Pendleside Limestone suggests a separate episode of dolomitization in
contrast to the lower part of the Pendleside Limestone dolomites.

Dedolomitization is another important diagenetic process that is encountered in the
Pendleside Limestone Group. This process suggests a shallow water environment and
nearness to surface conditions (Braun and Friedman, 1970) during which the ferroan
dolomite crystals attain an unstable stage and dedolomitization into ferroan calcite rhombs
as suggested by Al-Hashimi (1973) takes place. In order to account for this process and
the volume of the Pendleside Limestone Group which has been deposited a substantial
amount of basinal subsidence is suggested to have taken place. This supports George's

(1978) theory regarding a tectonic origin for the sediments deposited in the Dinantian subsystem.

Chapter Six

CHERTIFICATION

6.1   Introduction

6.2   Spatial distribution of chert throughout the Pendleside Limestone Group

6.3   Petrography of chert fabrics

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Chapter Six

CHERTIFICATION

6.1 Introduction

Chertification in carbonate strata has been the subject of voluminous literature dating back to at least the latter part of the nineteenth century, and continues today primarily under the stimulus of the Deep Sea Drilling Project. Research on cherts in intracratonic epeiric carbonates has included many fine field and petrographic studies (Choquette, 1955; Wilson, 1966; Banks, 1970; Folk and Pittman, 1971; Orme, 1974; and Meyers, 1977). However, the pre-1950's studies suffered from lack of understanding of silica solution chemistry and of carbonate depositional and diagenetic processes, and the bulk of these and later works have failed to answer the basic questions of timing, silica source, distributional controls and diagenetic environments of chertification.

Banks (1970) invoked chertification at the water table as the origin for the cherts in the Leadville Formation (Mississippian), but he did not use this to explain the stratal nature of cherts. Orme (1974) described the cherts, quartz rock, quartoze limestones, and a variety of discriminate and indiscriminate small-scale replacements of limestone components in the Viséan Limestones of Derbyshire. Meyers (1977) argued strongly for fabric control of chert distribution, which in turn is probably a function of the distribution of sponge spicules in the Lake Valley Formation in the Mississippian limestones of Sacramento Mountains, New Mexico.

In the Craven Basin, chertification has played an important role in promoting diagenetic processes and in producing new fabrics in the limestones and dolostones of the Pendleside Limestone Group. It is only found in the "peloidal or oolitic" limestones as

indicated by the petrographic examination of thin sections.

6.2 Spatial distribution of chert throughout the Pendleside Limestone Group

One of the prominent lithological features in the Pendleside Limestone is the chert bands. These occur in the upper two thirds of the Pendleside Limestone Group. They are hard, compact and dark grey in colour, sometimes displaying nodular features with sharp boundaries within the limestones (Plates 6.1C and 6.2A). During the field work it was observed that these chert bands increase in thickness and number at the top of the succession, especially when the unconformity between the Pendleside Limestone and Bowland Shales is approached.

On Pendle Hill and in section 1200, the chert bands are very prominent features of the Pendleside Limestone Group (Plate 6.1A and B). They are sometimes parallel to undulating or contorted laminae as observed in Plate 6.1A. In the Hodder River section (100) the chert bands are nodule-like (Plates 6.1C and 6.2A), although sometimes the bands show signs of termination (Plate 6.2A). In the Lothersdale area, in section 1800 the chert bands are also prominent (Plate 6.2B and C), they also display nodule-like features (Plate 6.2B) although sometimes they occur as bands terminating into one body as in Plate 6.2C.

It is observed that these chert bands always occur in coarse grained limestone deposited in shallow water and in the localities situated away from the basin centre. In the Salterforth section (PL+RW) the chert bands disappear where the shaly limestones and shales are fine grained in terms of textures.

6.3 Petrography of chert fabrics

Petrographic examination of thin sections in the Pendleside Limestone Group has revealed four major types of silica. These types are i) Microquartz; ii) Length fast (LF) chalcedony; iii) Megaquartz; Length slow (LS) chalcedony.

i) Microquartz, composed of crystals (anhedral in shape and less than 10 μm in size) that make up the bulk of the cherts in grain supported rocks. It includes pseudomorphs of calcite mud, crinoids, bryozoans, brachiopods, and corals. This proves that it is a replacement and not a cement (Meyers, 1977) (Fig. 6.1C) (Plate 6.3A and B). There is a crude order of susceptibility of carbonate fabrics to replacement by microquartz in the Pendleside Limestone Group. Least susceptible to replacement are syntaxial calcite cement rims on crinoids, followed by crinoids. Within a chert mass, typically all other skeletal grains are chertified yet crinoids and their syntaxial cements commonly remain largely unreplaced, or only partly replaced. Thick brachiopod shells may remain only partially replaced along with the crinoids. Most susceptible to replacement are small thin-shelled brachiopods, bryozoans, and mud. These all have about the same susceptibility and within chert masses are usually totally replaced.

ii) Length fast (LF) chalcedony occurs most commonly in interstices in skeletal grain-supported rock, i.e. peloidal limestones, where it forms more or less isopachous coatings on pore walls. The LF chalcedony often coats the edges of calcite crystals syntaxially on crinoids, where it mimics the surface, but contains its own botryoidal and/or isopachous growth lines. The edges of calcite crystals or peloids are interpreted as free growth surfaces of grains in the limestone framework (Evamy and Shearman, 1965, 1969; Meyers, 1974, 1977) (Fig. 6.1B, Plate 6.3C). The botryoidal pattern of the LF chalcedony is not a pseudomorphed calcite crystal growth pattern but rather a cement deposited on free surfaces of grains. LF chalcedony also occurs as a filling of intra-fossil cavities

where it again occurs as a more or less isopachous coating of the cavity walls, and/or hemispherical fans anchored on the walls of sediments.

The above features plus the fact that LF chalcedony never pseudomorphs skeletal grains, carbonate cements, or mud, never interrupts carbonate fabrics, and never contains undigested relict carbonate inclusions, prove that LF chalcedony is a cement and not a replacement.

iii) Megaquartz is the third major chert fabric. This type consists of mosaics of quartz crystals that are anhedral in shape and between 10 - 50 μm in size. It was called drusy quartz mosaic by Orme (1974). Generally the mosaic comprises equant rather than markedly elongated crystals. The megaquartz sometimes occurs as a void filling cement of minor volumetric importance throughout the Pendleside Limestone Group. This is indicated by the absence of carbonate inclusions within some of the megaquartz cement.

In some cases it pseudomorphs and replaces ferroan calcite cement. The evidence for the megaquartz as a replacement is that it contains minute inclusions of the host rock (carbonates) or transgresses the depositional fabric. In the cementing megaquartz the crystals are devoid of any inclusions and they do not invade or pseudomorph skeletal grains (Fig. 6.1B; Plate 6.3A and B).

iv) The last type of chert is the length slow chalcedony which occurs as replacements of shell cavities in brachiopods, as irregular blebs partly replacing some crinoids, and as inner replacement of some ooids (Fig. 6.1A; Plate 6.4A, B and C; Plate 6.5A). Evidence that the LS chalcedony is replacements and not cements is the fact that the inner core micrite in the ooids and peloids shows pseudomorphous replacement which contains minute carbonate inclusions (Plate 6.4A). The foregoing observations indicate clearly that chert fabrics can be identified as being cements or replacements. Furthermore chertification

has preserved some of the fine textures and fabrics in the limestones as ghosts, i.e. ooids and peloids (Plate 6.5B and C) or has destroyed completely all the features and outlines of the pre-existing limestone fabric.

Folk and Pittman (1971) considered the occurrence of LS chalcedony in large quantities as solid evidence for vanished evaporites. The LS chalcedony in the Pendleside Limestone does not indicate the former existence of evaporites because it occurs in very small quantities and there is no evidence of evaporite inclusions in the LS chalcedony. Furthermore the sedimentological evidence is inconsistent with the presence of evaporitic depositional environments in the Pendleside Limestone Group.

6.4   Geochemical environment of formation of chert varieties

6.4.1   Textural relationship with carbonate cements

Petrographic examination of silicified limestones and dolostones reveals that two distinct diagenetic episodes of chertification can be recognized in the Pendleside Limestone Group. The first episode took place prior to the deposition of ferroan calcite cement, whereas the second episode of silicification took place after the precipitation of the ferroan calcite.

A)   Pre-ferroan calcite silicification   Evidence for pre-ferroan calcite silicification is seen in silicification of allochems prior to ferroan calcite cementation. LS chalcedony and some microquartz are the only forms of silica precipitated at this stage of diagenesis. Some of the skeletons show replacement of micrite by microcrystalline quartz. The silicified skeleton floats in a ferroan calcite cement (Plate 6.6A, B and C). On the other hand, some ooids and peloids have their cores replaced by LS chalcedony. These ooids and peloids also float in a matrix of ferroan calcite cement. The relationship of

floating skeletons, ooids, and peloids in a ferroan calcite cement (Plate 6.7A) suggests their silicification prior to the cementation by ferroan calcite. If silicification occurred after ferroan calcite cementation (as in some other cases, Plate 6.6A, B and C) the whole rock (framework and cement) would have been silicified and not only the framework grains (Plate 6.7A).

B) Post-ferroan calcite silicification   Microcrystalline quartz, megaquartz and LF chalcedony are the predominant type of silica after the ferroan calcite cementation. Microcrystalline quartz forms the bulk of the chert and fills cavities and replaces both cement and skeletal parts. Evidence of replacement by microcrystalline quartz includes the fact that microcrystalline quartz pseudomorphs some of the skeletal parts and allochems and also invades the framework carbonate grains. The occurrence of carbonate inclusions in the microcrystalline quartz (Plate 6.7B and C) provided further evidence of its replacive origin.

The LF chalcedony rims the free surfaces of skeletons and allochems, e.g. ooids and peloids, and forms cementing fabric. No pseudomorphs or invasion of LF chalcedony is observed in the rocks of the Pendleside Limestone Group. Nor are any inclusions found in the LF chalcedony, whereas in the megaquartz crystals which occlude the cavities in between the allochems, carbonate inclusions are found. This suggests that megaquartz replaced the pre-existing cement as indicated by the inclusions (Plate 6.7B and C). In some of the rocks the chertification process is so pervasive that all the ghost fabrics are completely eradicated by microcrystalline quartz.

6.4.2   Geochemistry of formation of chert

Folk and Pittman (1971) discussed the chemistry of formation of LS chalcedony, megaquartz, microcrystalline quartz and LF chalcedony.

As with most other minerals, the main control on the gross morphology and crystal size of quartz is the rate of nucleation and crystallization which in turn is largely dependent on saturation (Folk et al., 1952; Oldershaw, 1968). Thus we find that in silicified limestones, microcrystalline quartz (equant crystals) which forms the bulk of the silica, developed first and probably most rapidly. Cavities, on the other hand, are lined first with fibrous chalcedonic quartz (two small one large dimensions) precipitated at some intermediate rate, and finally the terminal filling of the cavity is equant megaquartz (three large dimensions), precipitated at the lowest rate. Presumably this sequence is due to slower and slower precipitation as the access to cavity by silica-rich solutions is gradually closed off.

Iler (1955), Millot et al. (1963) and Alexander (1967) referred the formation of LS and LF chalcedony to the variation in pH and concentration of silica in solution. At a high pH, silica in solution tends to be more ionized, while at neutral or low pH it is combined into $Si(OH)_4$ groups. At neutral or low pH and high concentrations, these groups polymerize. At a high concentration and high pH, silica precipitates (Fig. 6.2) and should take a fibrous chalcedonic form (Folk and Pitman, 1971) because of the rapid rate of formation. Because of the high pH, silica will however occur as more ionized single tetrahedra these can set themselves down one by one on the crystal surface (Fig. 6.3B). Thus, since they precipitate out singly, they easily take the correct orientation of ordering quartz, i.e. with c-axis parallel with the long axis, just as they would in a more slowly-growing crystal of ordinary quartz. This results in length slow chalcedony which grades into megaquartz then into perfectly ordinary large crystals of quartz with good crystal terminations (Folk and Pitman, 1971).

At a high concentration and low pH, silica should precipitate rapidly and assume the fibrous morphology. But since at this pH the material is polymerized, the orientation

is not that of quartz. Presumably the polymers will take the form of spiraling chains of silica tetrahedra parallel to the c-axis. If these spiral chains of tetrahedra are accumulating upon a surface, they will lie down flat-wise on the surface of the grains (Fig. 6.3A). Thus chalcedony formed at neutral or low pH will have the c-axis lying tangentially to the surface, and perpendicular to the direction of growth of the fibres. Accumulation of length fast chalcedony as tangential chains of silica polymers in a disordered brush-pile fashion means that a lot of impurities, particularly water, may be trapped; this is responsible for the brown colour of chalcedony and the low refractive index (Folk and Weaver, 1952; Oldershaw, 1968). Folk and Pittman (1971) suggested that replacement of ooids and peloids favours length slow chalcedony, while nearly all length fast chalcedony forms as a cavity-filling. They mentioned that if fibrous silica is replacing a carbonate, it will be relatively easy for single ionized silica tetrahedra to float in along the water-filled interface between silica and the mineral being replaced, and that chains of polymerized silica would find this much more difficult. Thus LS chalcedony would be the kind usually produced by replacement of carbonate minerals.

The diagenetic environment of formation can thus be deduced from the type of chalcedony precipitated at each episode. The LS chalcedony in the Pendleside Limestone Group is postulated to be pre-ferroan calcite cementation due to its textural relationship with the ferroan calcite cement (Plates 6.4C and 6.5A). Since LS chalcedony precipitation favours a high concentration of silica and neutral or high pH then it seems likely that the solution during this earlier phase of silicification contained high concentrations of silica and was of neutral or high pH. Also the replacement of cherts by LS chalcedony is much easier with LS chalcedony than LF chalcedony for the reasons mentioned above.

As for the LF chalcedony, it is suggested that it is a post-ferroan calcite cementation process as indicated by its textural relationship with the ferroan calcite cement.

High concentration of silica and neutral or low pH of solution is favoured for the formation of LF chalcedony. This again reflects the environments of diagenesis of post-ferroan calcite cementations as a high silica content and neutral or low pH of solution.

6.5 Silica source

Spicule diagenesis seems to have a positive relationship to chertification as revealed by petrographic examination of silicified limestone specimens. Abundance of calcitized siliceous spicules near silicified zones in the Pendleside Limestone suggests that the dissolved siliceous spicules were the main source of silica in the chertification process.

Modern spicules are of two major compositional types, siliceous and $CaCO_3$. Silica spicules comprise biogenic opal (X-ray amorphous opal), and all contain a well-developed central axial canal. Carbonate spicules are single crystals with no axial canal and most of them are of a high-magnesium calcite with about 7% $MgCO_3$. More rarely they are aragonite (Meyers, 1977).

In the Pendleside Limestone Group, spicules are of two types, calcitic and siliceous. Most of the calcitic ones are multicrystalline moulds, some of which are partially silicified (Plate 6.8A and B). Rarely, unaltered siliceous spicules are found. These contain a well-developed axial canal and an outer zone of clear, radial fibrous silica. These are interpreted as original siliceous spicules by analogy with modern spicules. Most of the calcitic spicules consist wholly of calcite with no evidence of an axial canal and show a typical neomorphic fabric. These are interpreted as multicrystalline calcite-filled moulds of former siliceous spicules, cut such that the cross section lies within a single crystal. These spicules range in size from 1.5 mm up to 3.0 mm. Some of the siliceous spicules, although very rare, are still undissolved and retain their original texture. These siliceous spicules in the Pendleside Limestone Group are common in and near chert zones.

A reasonable sequence of events of spicule diagenesis is as follows:-

On the sea floor at least some of the spicules began dissolving as indicated by their enlarged canals which may be filled with lime mud and occasionally with authigenic pyrite (Plate 6.8C). During early stages of burial, incipient calcite cementation filled some canals, and perhaps caused lithification of the lime mud fills in others. Spicules were then dissolved, most of the resultant moulds retaining no sign of former canals. Continued burial led to compactional distortion of moulds and shifting of some canal pseudomorphs. Many moulds, perhaps most, were completely destroyed. Next, silica replaced lime mud in canals and in host matrix, and filled the moulds, in some cases with silica cement. The silica cement is thought to be derived locally and not from a distant source due to the following:-

The silicification of the limestone horizons is selective only to some of the coarse grained allochemical limestones, e.g. ooids and peloids, and it is always associated with the dolomitization. This is indicated by the coexistence of dolomite rhombohedra in a siliceous matrix. If the silica was derived from a distant source it would have chertified all the allochemical limestones, but this is not the case. This suggests that the source of silica is limited and that the silicification would stop in the case of complete consumption of the silica source.

The foregoing observation suggests that the source of silica in the Pendleside Limestone Group is derived locally and not from a distant source.

6.6   Some geochemical aspects of the chertification process

Silicon concentration throughout the Pendleside Limestone Group was determined by atomic absorption spectrophotometry, and the concentrations in parts per million are tabulated in Table 6.1 for each analysed section. The silicon is concentrated in the

Group during silicification.

In Fig. 6.4 the silica concentration increases towards the top, especially in the localities where the unconformity is most prominent. This is clearly seen in S. 1200, S. 1300, S. 1500 and S. PL+RW (Fig. 6.4) to the east of which the unconformity is well-developed. To the west and in the Hodder River section (100) the silica decreases towards the top relative to the forementioned sections. The unconformity is poorly developed and not seen in that part of area.

In the Slaidburn area and in S. 200, S. 300 and S. 800 (Fig. 6.6) the silica shows a remarkable increase towards the northeast where the unconformity is well-developed towards the southern edge of the Askrigg Block.

6.7 Proposed mechanism responsible for the chertification process

The following observations are relevant in the process of chertification of the carbonates in the Pendleside Limestone Group:

1) Length slow chalcedony is deposited in the first episode of chertification. This is indicated by the textural relationship of the LS chalcedony with the host rock; and the formation of LS chalcedony needs a high concentration of silica and a high pH of solution (Folk and Pittman, 1971) which can be provided at the pre-burial phase, during sedimentation, when the sediments are still in contact with sea water (Tracey, 1971; Deep sea drilling project).

2) The second episode of chertification which consists mainly of LF chalcedony, microcrystalline quartz, megaquartz and sometimes pre-existing LS chalcedony; these are always associated with dolomites.

chertified limestones and to a lesser extent in the diagenetic feldspars, quartz and clays. However, the silica in the authigenic feldspars, quartz and clay constitutes only a negligible amount as revealed by X-ray diffraction compared to the chertified limestones.

The silica concentration values in Table 6.2 were processed using computer program SYMAP in order to characterize the vertical and lateral concentration of silicon throughout sections 100, 400, 1200, 1500 and PL+RW (Fig. 6.4). The silicon concentration pattern shows a periodical increase and decrease throughout the map from top to bottom. These increases in silica concentration correspond to the occurrence of peloidal limestone horizons throughout the Pendleside Limestone Group. This feature suggests that silicification was selective to coarse grained allochemical limestones rather than fine grained limestones.

The silica concentration also shows an inverse relationship with the Ca^{+2} ion concentration. The Ca^{+2} ion concentration (ppm) was determined by atomic absorption spectrophotometry (Table 6.1). The Ca^{+2} ion concentration was also processed using SYMAP computer program and the resultant map is shown in Figure 6.5, which represents the Ca^{+2} concentration in S. 100, S. 400, S. 1300, S. 1500 and S. PL+RW. Comparisons of silicon concentration (Fig. 6.4) with Ca^{+2} ion concentration (Fig. 6.5) shows an inverse relationship of both elements with each other. This is to be expected in limestones which were silicified during diagenesis. A similar analysis was carried out for sections 200, 300 and 800 in the Slaidburn area (Tables 6.3 and 6.4). The silicon ion distribution pattern shows periodic increase and decrease throughout the Pendleside Limestone Group from top to bottom (Fig. 6.6). A marked inverse relationship between the Si^{+4} ion concentration and the Ca^{+2} ion concentration (Fig. 6.7) is also seen. This is also postulated to be due to the replacement of Ca^{+2} by Si^{+4} ions in the Pendleside Limestone

3) Silica and calcite dissolve in a low pH solution and a low concentration of both elements in solution (Blatt et al., 1972) (Fig. 6.2).

4) As the concentration of both elements increases and pH is still low only silica precipitates, whereas the calcite remains dissolving (Fig. 6.2).

5) Gathering the forementioned observations and in view of the fact that dolomite rhombs and ferroan calcite coexist together in a matrix of chert the following mechanism is suggested:-

The dolomitization process is initiated by the mixing of fresh and sea waters in the phreatic zone. The dolomitization is a pre-ferroan calcite cementation process as indicated by the textural relationship (Chapter 5). Then there was a period of ferroan calcite cementation which continued contemporaneously with the dolomitization process during which silicification in some dolomite horizons also took place. The silicification process here was initiated by the same dolomitizing solutions because these solutions had a low pH value (fresh waters) which dissolved the siliceous material and continued dissolving them until a high concentration of silica was attained (Fig. 6.2) and the pH was still low. In this low pH of solution, the calcite was still dissolving whereas the silica started to precipitate (Fig. 6.2) as varieties of cherts each according to its position in the depositional site, e.g. LF chalcedony on free surfaces. The relationship between the process of chert precipitation and ferroan calcite dissolution is clearly indicated in the thin section examination (Plate 6.7A, B and C) where relict calcite and dolomite rhombs float in a chertified matrix.

6.8 Discussion and conclusions

Chertification is another important diagenetic process which produced new diagenetic

fabrics and provides a good picture of the sequence of events that took place in the Pendleside Limestone Group. The new fabrics created by the chertification process are:-

1) LS chalcedony which replaces the cores of ooids, peloids, echinoderm plates, and crinoid stems. The pseudomorphism of the LS chalcedony indicates the replacive origin of this mineral. This is also suggested by the numerous carbonate inclusions within the replaced host.

2) LF chalcedony, which rims the free surfaces of allochemical grains, indicates that it is a cement and not a replacement. This is further confirmed by the absence of carbonate inclusion in the LF chalcedony; the LF chalcedony never intrudes, cuts, or pseudomorphs any surrounding grains.

3) Microcrystalline quartz which replaces the pre-existing ferroan calcite cement. This is indicated by the inclusions of the carbonate host and the textural relationship between microcrystalline quartz and ferroan calcite.

4) Megaquartz which also replaced the pre-existing ferroan calcite cement as indicated by carbonate inclusions and textural relationships.

The first episode of chertification took place prior to burial, perhaps during sedimentation, during which the sediments were still in contact with sea water. The textural relationships of the LS chalcedony which replaces some of the cores of peloids, ooids, some echinoderms and crinoid stems clearly indicate that the chertification process was an early diagenetic replacement. This process involved a high pH of solution (Folk and Pittman, 1971) and a high concentration of silica which was provided by the dissolution of siliceous spicules at the time. The LS chalcedony could not have been precipitated at a later stage simply because the solution pH during the second episode of silicification was low. Besides the textural relationships of LS chalcedony with the ferroan calcite cement and its

solitary occurrence in the ferroan calcite matrix suggests that it was deposited in a separate episode.

The second episode of chertification consists of LF chalcedony, microcrystalline quartz, megaquartz and sometimes the pre-existing LS chalcedony in the cores of the peloids and ooids. The textural relationship of the second episode of cherts suggests that they have formed during and after the ferroan calcite cementation and replaced the ferroan calcites as revealed by the petrographic examination of thin sections (Plates 6.7A, 6.9A). The chemistry of deposition of LF chalcedony suggests a high concentration of silica and a low pH of solution (Folk and Pittman, 1971). This coincides with the fresh water impulse that mixed with the trapped sea water to dolomitize the limestones. The fresh water has a low pH and is capable of dissolving the siliceous spicules which are postulated to be the source for silica. The calcite spicules are found abundantly in the Pendleside Limestone Group. The morphology of the spicule suggests that they were originally siliceous because they contained the central canal (Meyers, 1977) as in present-day siliceous spicules. These spicules were dissolved, some of them completely, to provide the necessary source for silica in the chertification process.

CHAPTER SEVEN

Chapter Seven

CONCLUSIONS

The Pendleside Limestone Group (Asbian) of the Craven Basin consists of a sequence of alternating shales, bioclastic limestones and dolostones which were deposited in a shallow, continuously subsiding basin. The sediments are considered to be distal turbidites which were deposited as large submarine fans derived turbidites from a northerly source area, the Askrigg Block. Some sediments are considered to be non-turbiditic interfan deposits. Proximal turbidite equivalents with submarine breccias are represented by the Pendleside Limestone of the Slaidburn area and the Draughton Limestone of the Skipton area.

Field observation, petrographic examination of thin sections, and analysis of the spatial distribution of sediments in the basin of deposition led to the following conclusions:

Continuous turbiditic sedimentation resulted in sediment-accumulation up to, and above, the wave base. At this point the formation of peloidal and/or oolitic limestones took place due to sediment reworking. Contemporaneous with sediments accumulation from turbidity currents, the Mid-Craven Fault was active and caused periodic subsidence of the basin floor. This resulted in the lowering of the plane of deposition beneath the wave-base. This in turn brought about the deposition of shales in a quiet water environment which was subjected to periodic influxes of carbonate detritus by turbidity flows. Up to ten such cycles of sedimentation have been recognized in the Pendleside Limestone Group.

Diagenesis had a great influence on the rocks comprising the Pendleside Limestone

Group from the time the sediments were deposited up to final lithification. The relative age of the diagenetic changes is early (during the deposition of the Pendleside Limestone) rather than late and final lithification was accomplished prior to the onset of sedimentation in the succeeding (Brigantian) Stage.

Petrographic observations indicate that the diagenetic processes brought about new fabrics and created new minerals which replaced the depositional texture and original mineralogy of the Pendleside Limestone Group. Some of the diagenetic changes involved were cementation, dissolution, authigenesis and replacement, including dolomitization. The cementation involved some alteration of framework constituents, it also brought about granular cementation and syntaxial overgrowth (rim cementation) of some of the framework constituents. Other features such as pressure-solution (including grain to grain pressure solution and stylolitization) have also been involved in the alteration of rock masses. Dissolution of carbonates was observed in the Pendleside Limestone Group and this was essential in providing carbonate ions necessary for the dolomitization process. Two types of dissolution were observed, selective and non-selective. Selective dissolution involved partial dissolution of parts of fossils, i.e. aragonitic parts, whereas non-selective dissolution involved the dissolution of high Mg-calcite to be replaced by ferroan calcite or non-ferroan calcite.

Authigenesis was an important process in the Pendleside Limestone Group which involved the formation of authigenic feldspars and authigenic quartz. The limitation of authigenic feldspar (albite) to the lower part of the Pendleside Limestone succession and the geochemistry of feldspar-bearing horizons is of significance regarding the origin of the authigenic albite. The geochemical results showed that the spatial distribution of elements such as aluminium, potassium and sodium revealed a close, positive relationship to the spatial distribution of shales. This led to the conclusion that the source of the

aluminium silicates which formed the albites was in the clay minerals (kaolinite and illite) found in shales. The sodium distribution coincides with the distribution of the authigenic albites throughout the Pendleside Limestone Group. The conclusion is supported by textural evidence: authigenic albite is most abundant in limestones which are in close proximity to shale beds.

Authigenic quartz grains are distributed throughout the Pendleside Limestone succession, unlike the authigenic feldspars. Some of the silica is thought to have been from siliceous spicules which dissolved during diagenesis.

Replacement of a mineral by another took place on a large scale in the sediments of the Pendleside Limestone Group. Two main processes are involved: dolomitization and chertification. Dolomitization is the most prominent diagenetic process that the Pendleside Limestone has undergone. This process created remarkable textural and compositional changes of the original fabric throughout the Pendleside Limestone Group. Petrographic examination of thin sections has revealed that in many cases the original depositional fabrics have been completely obliterated by dolomitization. In some cases ghost textures are still visible. The dolostones are variable both texturally and compositionally. They generally show a hypidiotopic-poikilotopic fabric in the lower part of the Pendleside Limestone Group and are almost all ferroan dolomites. In the upper part of the Pendleside Limestone the dolostones are generally non-ferroan although a few ferroan dolomite rhombs occlude the pore spaces. Also, some of the dolomite rhombs in the upper part of the Pendleside Limestone Group are idiotopic-poikilotopic, rimmed with iron oxide and in a few cases by ferroan dolomite. Structural variation of dolomite rhombs has also been found to be variable. Some dolomite rhombs are perfectly ordered dolomites and very close to ideal dolomite composition (1:1 Ca:Mg ratio). In these dolomites the set of planes parallel to the a and c crystallographic axes is perfectly developed and

tend to have a perfect order of reflection. These dolomite rhombs are found in the upper part of the Pendleside Limestone succession. In the lower part of the succession most of the dolomite rhombs tend to have poor order of reflection. This is because the set of planes parallel to the a and c-crystallographic axes is poorly developed. The composition of these dolomite rhombs is far from the ideal dolomite composition and tends to be calcium rich. The reasons responsible for such a disordering of the dolomite rhomb are the occurrence of foreign ions, e.g. iron or manganese within the unit cell of the dolomite rhombs, or the occurrence of excess $CaCO_3$ within the dolomite structure. Intergrowths of the dolomite rhombs also create such a disordering of the unit cell. Microprobe analyses of some dolomite rhombs revealed some compositionally variable dolomites. Some of the dolomite rhombs have a ferroan core whereas others were devoid of the ferroan cores; nearly all the dolomites proved to be calcian in composition.

Porosity is developed through the dolomitization process due to the higher density of dolomite compared to calcite. Also the shape and orientation of the dolomite rhombs creates porosity zones around the rhombs as revealed by scanning electron microscopy. Another process which brought about porosity was the dissolution of calcite which provided the carbonate ions necessary for the growth of dolomite rhombs. The source for carbonate ions is thought to be local rather than distal. This is due to the development of high percentage of porosity around the dolomite rhombs thus increasing the permeability of the dolomitized rock.

Geochemical analyses of magnesium, iron, strontium, and manganese showed some variation in conjunction with the dolomite distribution throughout the Pendleside Limestone Group. The application of computer program SYMAP revealed some high concentration zones of magnesium that are not dolomitized, whereas in other parts the magnesium is mainly concentrated in the dolomitized zones. The reason for this discrepancy probably

lies in the fact that some limestones contain abundant micro-dolomite inclusions, particularly within calcite crinoid fragments, which formed as a result of the inversion of high-magnesian to low-magnesian calcite. Magnesium was thus trapped in these limestones but in such small crystals, and small quantities as to be undetected by X-ray diffraction.

Strontium concentration is very low in the limestones of the Pendleside Limestone Group compared with the strontium concentration in Recent seas. This suggests the prevalence of an open system through which large volumes of fluid percolated and removed the strontium. The strontium concentration is found to have an inverse relationship with the intensity of dolomitization.

Iron is mainly concentrated in ferroan dolomites, ferroan calcites and iron oxide. The distribution of this element throughout the Pendleside Limestone Group is found to be closely associated with the distribution of shale beds. Thus the concentration of iron is much higher in the lower part of the Pendleside Limestone succession rather than the upper parts.

The manganese concentration is found to have a positive relationship with the intensity of dolomitization. Thus it tends to increase in intensely dolomitized zones and decrease where no dolomitization occurs.

Dolomitization varies in intensity throughout the Pendleside Limestone Group from 1.0 wt. % to 100.0 wt. %. Up to ten zones have been identified which generally increase in intensity and thickness towards the top of the Pendleside Limestone. The topmost part of the Pendleside Limestone is thus completely dolomitized in places. The dolomite zones also bear a close relationship to coarser grained lithologies which were deposited during episodes of shallow water sedimentation.

The spatial distribution of dolomitized zones, textural relationships, and geochemical

variation suggest that dolomitization took place in a phreatic lens of mixed sea water and fresh water. This explains why many of the dolostones are ferroan and why the concentrations of Sr^+ and Na^+ are so low. The extension of fresh water from land areas and their mixture with sea water trapped in pore spaces in the phreatic zone is also the best means of explaining the spatial distribution of dolostone bodies. The process took place during periods of maximum deposition of sediments prior to subsidence when the sediments were in proximity to the phreatic zone. This is indicated by the confinement of dolomite to peloidal limestone beds which are considered to be indicators of the critical thickness of sediments prior to subsidence. This type of mechanism also accounts for the alternation of dolomitized and undolomitized zones throughout the Pendleside Limestone Group. It also suggests that the dolomitization in the Pendleside Limestone took place early during diagenesis and in many episodes. In contrast, the evidence is less consistent with other mechanisms of dolomitization such as hypersalinity or seepage-reflux. In the former case there is no indication of associated evaporites and in the latter no evidence of a reflux barrier.

Dedolomitization is another diagenetic process that took place subsequent to dolomitization. It created new fabric (polycrystalline calcite rhombs) and indicated a pronounced change in the environment of carbonate diagenesis. The metastability of ferroan dolomite near surface conditions is due to the presence of Fe^{+2} ions in the lattice of the ferroan dolomite and the occurrence of excess $CaCO_3$. This brought about dedolomitization of the ferroan dolomite rhombs. The occurrence of dedolomite suggests nearness to surface conditions and prevalence of oxidizing environment as indicated by the oxidized dedolomite rhombs. Dedolomites were found only in one horizon throughout the Pendleside Limestone Group.

Chertification of the carbonates (calcite and dolomite) is another, mainly replacive,

process which is intimately associated with the dolomitization of the Pendleside Limestone Group. Cherts occur in thin beds (2 cm to 10 cm in thickness) and nodule-like masses throughout the succession but are particularly concentrated in dolostones towards the top of the Pendleside Limestone Group. Four major types of chert have been encountered:

A) Microquartz - which is composed of crystals that make up the bulk of the cherts in grain-supported rocks. It consists of pseudomorphs of calcitic mud, crinoids, bryozoans, brachiopods, and it is thus considered as a replacement and not a cement.

B) Length fast chalcedony - which occurs most commonly in interstices in skeletal grain-supported rocks, for example peloidal or oolitic limestones, where it forms more or less isopachous coatings on the walls of interstices. The botryoidal pattern of the length fast chalcedony is not a pseudomorph of calcite and it is considered to be cement, due to its growth on free surfaces of grains. Other evidence that the length fast chalcedony is a cement includes the absence of host (carbonate) inclusions and the fact that it never intrudes or interrupts carbonate depositional fabrics.

C) Megaquartz - which consists of mosaic of equant quartz crystals. The megaquartz is sometimes a void filling cement, whereas in other cases it pseudomorphs and replaces the carbonates. Pseudomorphism and replacement of carbonates by megaquartz is indicated by the presence of inclusions of the host (carbonates) and its invasion of some skeletal grains.

D) Length slow chalcedony - which occurs as a replacement of some ooids. Length slow chalcedony is considered to be a replacement rather than a cement due to the presence of carbonate inclusions.

The geochemical environment of formation of chert varieties varies according to the

type of chert. Length slow chalcedony is postulated to form at a high concentration and high pH solution because in these conditions silica tends to ionize into single fibres thus forming the length slow chalcedony. By contrast in a high concentration and a low or neutral pH silica tends to polymerize and forms length fast chalcedony which is a polymerized form of silica. The final product of chertification in which all the varieties of silica will end is the megaquartz and the microquartz. This is dependent on the maturity of the diagenetic processes at the time.

The source for silica in the Pendleside Limestone Group is considered to be the dissolution of siliceous spicules. Spiculitic lithologies are abundant throughout the Pendleside Limestone Group. In most cases the spicules are moulds filled with ferroan calcite and their original mineralogy cannot be determined. In other cases there are siliceous spicules, some partly replaced by calcite, which contain a central axial canal indicating that they were originally siliceous sponge spicules (this canal is absent in Recent calcite spicules). It is possible that the majority of spicules in the Pendleside Limestone were originally siliceous. Dissolution of the spicules is thought to have occurred at about the same time, and under similar conditions, to the dolomitization process. The dissolution resulted in the remobilization of large quantities of silica in solution and its later reprecipitation as chert horizons.

The diagenesis of the Pendleside Limestone Group involved extensive mineralogical and textural changes which completely modified the original sediment. The evidence presented in this work suggests that these changes were brought about at a relatively early post-depositional stage and were an inevitable consequence of the stratigraphical and sedimentological variables.

APPENDIX A

The staining method for carbonate minerals

The method described is applied to thin sections(before covering) and polished slabs.

Peels were also made from stained slabs.

Weak acid solution was used a) reaction between the staining reagent and Ca^{+2}.

Fe^{+2} etc., producing distinctive colours as in the table below; b) rate of solution, and of

the reaction, timewise is also controlled and restricted to 20 seconds in the combined

stain and 10 seconds in the Alizarin Red S.

1) In calcites versus dolomite, Alizarin Red S or combined stain (3 parts

   of potassium ferricyanide) is used.

2) Ferrous iron in calcites or dolomites: potassium ferricyanide or

   combined stain is used.

Procedure used in preparing the stains

A) 1.5% HCl (1.5% of concentrated HCl in distilled water). 30 ml conc.

   HCl is added to 2000 ml of distilled water.

B) 0.2% Alizarin Red S in 1.5% HCl. 1.2 gram of Alizarin Red S is

   dissolved in 600 ml of 1.5% HCl.

C) 2% Potassium ferricyanide 4 gram of potassium ferricyanide is

   dissolved in 200 ml of 1.5% HCl.

D) Combined stain consists of solutions B and C in 3:2 proportions

   respectively.

Table for the reaction of common carbonates with the staining technique

Carbonate	Staining Components		Combined Result
	Alizarin Red-S	Potassium Ferricyanide	
Trigonal			
Rhodocrosite Mn CO_3	–	Very pale brown	Very pale brown
Magnesite Mg CO_3	–	–	–
Siderite $FeCO_3$	–	–	–
Ferroan Dolomite Ca (Mg Fe) $(CO_3)_2$	–	Pale to deep turquoise	Pale to deep turquoise
Dolomite Ca Mg$(CO_3)_2$	–	–	–
Ferroan Calcite $FeCa(CO_3)_2$	Pink to pale pink	Pale to deep turquoise	Mauve – purple – royal blue
Calcite Ca CO_3	Pink to pale pink	–	Pink to pale pink
Orthorhombic			
Aragonite $CaCO_3$	Pale pink	–	Pale pink
Witherite Ba CO_3	Red	–	Red
Cerussite Pb CO_3	Mauve	–	Mauve

Procedure of staining thin sections

1) Thin sections (uncovered) are etched in 1.5% HCl for 10 seconds.

2) Thin sections are then stained in the combined stain for 20 sec.

3) Thin sections are rinsed briefly in distilled water.

4) Thin sections are stained for 10 seconds in Alizarin Red S.

5) Then rinsed in distilled water, left to dry and covered.

APPENDIX B

Atomic Absorption Spectrophotometric Method of Analysis

Atomic absorption analysis was carried out on powder rock samples. A description of the procedure follows:-

1. Powdered rock specimen (0.2000 gram) is weighed, and mixed with a flux to prevent it sticking to the wall of the carbon crucible.

2. The sample and flux in the carbon crucible are put in the furnace for 15 minutes and in a temperature of 950°C.

3. Afterwards the molten sample and flux were put into 4% HNO_3 acid and stirred until the solute was completely dissolved into the solution.

4. The volume of 4% HNO_3 acid is completed to 100 ml.

5. All containers are of polythene type to prevent the adsorption of silica.

6. The solutions are analysed in the atomic absorption spectrophotometer of the Perkin-Elmer type 460. This type of analyser is built up to work with a lower and upper standard for each element, against which the instrument draws a curve and accordingly produces the result in parts per million. Blank sample is used for comparison and checking.

7. To determine the parts per million (ppm) in 0.2000 gram of a sample, the following equations are employed to substitute the results of the atomic absorption analyser:

    (Standard A) - (actual reading for standard A) = X_1

    (Standard B) - (actual reading for standard B) = X_2

    $$\frac{X_1 + X_2}{2} = Y \qquad Y = \text{mean of the standards}$$

    (Value read for the sample - Blank sample) (Y) = Z.

Element	Wavelength (nm)	Setting slit	Light source	Flame type	Standard A µg/ml	Standard B µg/ml
Na	589.6	0.7	Hallow Cathod Lamp	Air-acetylene flame oxidizing (lean-blue)	0.8	1.0
K	766.5	2.0	Hallow Cathod Lamp	Air-acetylene flame oxidizing (lean-blue)	0.04	2.0
Ca	422.7	0.7	Hallow Cathod Lamp	Air-acetylene flame oxidizing (lean-blue)	0.08	4.0
Mg	285.2	0.7	Hallow Cathod Lamp	Air-acetylene flame oxidizing (lean-blue)	0.01	0.5
Mn	279.5	0.2	Hallow Cathod Lamp	Air-acetylene flame oxidizing (lean-blue)	0.05	2.0
Sr						
Si	251.6	0.2	Hallow Cathod Lamp	Nitrous oxide acetylene flame Reducing (rich, red)	2.0	50.0
Fe	248.3	0.2	Hallow Cathod Lamp	Air-acetylene flame oxidizing (lean-blue)	0.1	5.0
Al	309.7	0.7	Hallow Cathod Lamp	Nitrous oxide acetylene flame Reducing (rich, red)	1.0	50.0

parts per million of element in 0.2000 gram of sample $= \dfrac{Z \times 100}{0.2000}$.

8. Specification for each element analysed in the atomic absorption spectrophotometer are in the table below.

APPENDIX C

SYMAP (short for Synagraphic Mapping) is a computer program for producing line-printer maps which generally depict spatially disposed quantitative qualitative information.

SYMAP originated from the Laboratory of Computer Graphics at Harvard University in the United States. The program was modified at the Edinburgh Regional Computer Centre to run on their IBM 360/50. It has been further modified at Hull University for use on ICL 1900 Range machines.

SYMAP is capable of producing three types of map on the lineprinter:-

1. Contour maps generally depict spatially continuous information such as most topography, rainfall, or population density. Contours (or isolines) are curves which connect points that have the same numerical value. The curves are inter-polated in such a way as to give a continuous slope between contours. SYMAP will produce a contour map from any set of values for a scattered distribution of points.

2. Conformant maps are best suited to qualitative or quantitative data which relates to spatial units whose areal limits are significant, and whose representation as a continuous surface is inappropriate.

3. Proximal maps are useful for displaying information, such as land use patterns, which are either quantitative or qualitative (i.e. descriptive) in nature and which may be discontinuous. The vertical and lateral distribution maps of the elements analysed in the atomic absorption spectrophotometer, is of this type of map.

Production of maps with SYMAP

A source (or base) map is first produced to a scale of 13 inch:25 kilometers. Areal outlines, data points and their associated values are all clearly marked.

SYMAP itself goes through all the stages that a cartographer either intuitively or consciously follows in producing a map. The information relating to each of these stages was specified by means of packages, which are simply sets of punched cards containing relevant data.

Each SYMAP package has a different category of information. The packages are assembled in the following order:-

1. A - outline package, in which the geographic area to be mapped is defined and outlined.

2. B - Data package, in which the location coordinates of all data points are established.

3. E - values package, which specifies the actual values to be assigned to the location.

4. F - Map package, which is the final package that produces the output map and it also is used to describe the size, scale and content of the output map, together with the class intervals and symbolism to be used.

Note: Blank areas in the map are areas of no data as explained in the SYMAP manual. Only the shaded areas are to be concerned to their assigned values.

MICROPROBE ANALYSIS

Microprobe analysis of some dolomitic limestones is carried out on the Cambridge microscan V instrument. Beam and sample current used is 10^{-6} amperes under an acceleration voltage of 15 kV. Crystal analysers used are (Lif) for Calcium, Iron and Manganese; (RAP) for Magnesium.

Thin sections of dolomitic limestones were prepared, highly polished, and then ultrasonically cleaned with either inhibisole or methylated spirits. Carbon coating of the thin section was used in a range of 3-5 microns to give a good electrical conductivity and reflection of the electron beam.

Many difficulties were encountered during the probe examination of the dolomite samples. These are:

1) The thickness of the thin section should be in the range of 50-60 microns. Sections thinner or thicker than the mentioned range cause the decomposition of the carbonates and even the bubbling of the specimen surface if the beam current is high. If bubbling or decomposition takes place, unavoidable errors will arise by the creation of charges on the surface of the sample, thus causing an inaccurate reading for the elements being analysed.

2) If there is any defect (depressions, projections) on the surface of the sample (as a result of poor polishing) this will affect the reading and yield inaccurate results. Highly polished thin sections are desirable to avoid such a possibility.

3) The setting of the probe units should be at a maximum regarding each and every

unit to give the maximum reading of the sample. For example, the beam current should be set at the peak of the current to give maximum readings and the Bragg angle for each element should be set to give a maximum reading of the element in the sample.

4) The standard should be highly polished and repolished periodically to avoid the formation of an oxide filming on the surfaces.

The formation of the oxide film on the surfaces will affect the readings of the standreds. Consequently, it will affect the reading of the percentage of the element being analysed in the sample according to the formula below which is used to determine the percentages of each element:

$$\text{Element } \% = \frac{\text{Reading of the sample } - \text{Background reading of the sample } + \text{Lost counts}}{\text{Reading of the standard } - \text{Background reading of the standred } + \text{Lost counts}}$$

The lost counts could be measured from the curve below for the sample and standard The resultant percentages of each element are put into a computer program in order to correct each element relative to its percentage within the rock

MICROSCAN V DEAD TIME (2.0 μ SECS)

[0 - 22000 cps]

[22000 - 110000 cps]

COUNT RATE

LOSTCOUNTS

800

700

600

500

400

300

200

100

2000   4000   6000   8000   10000   12000   14000   16000   18000
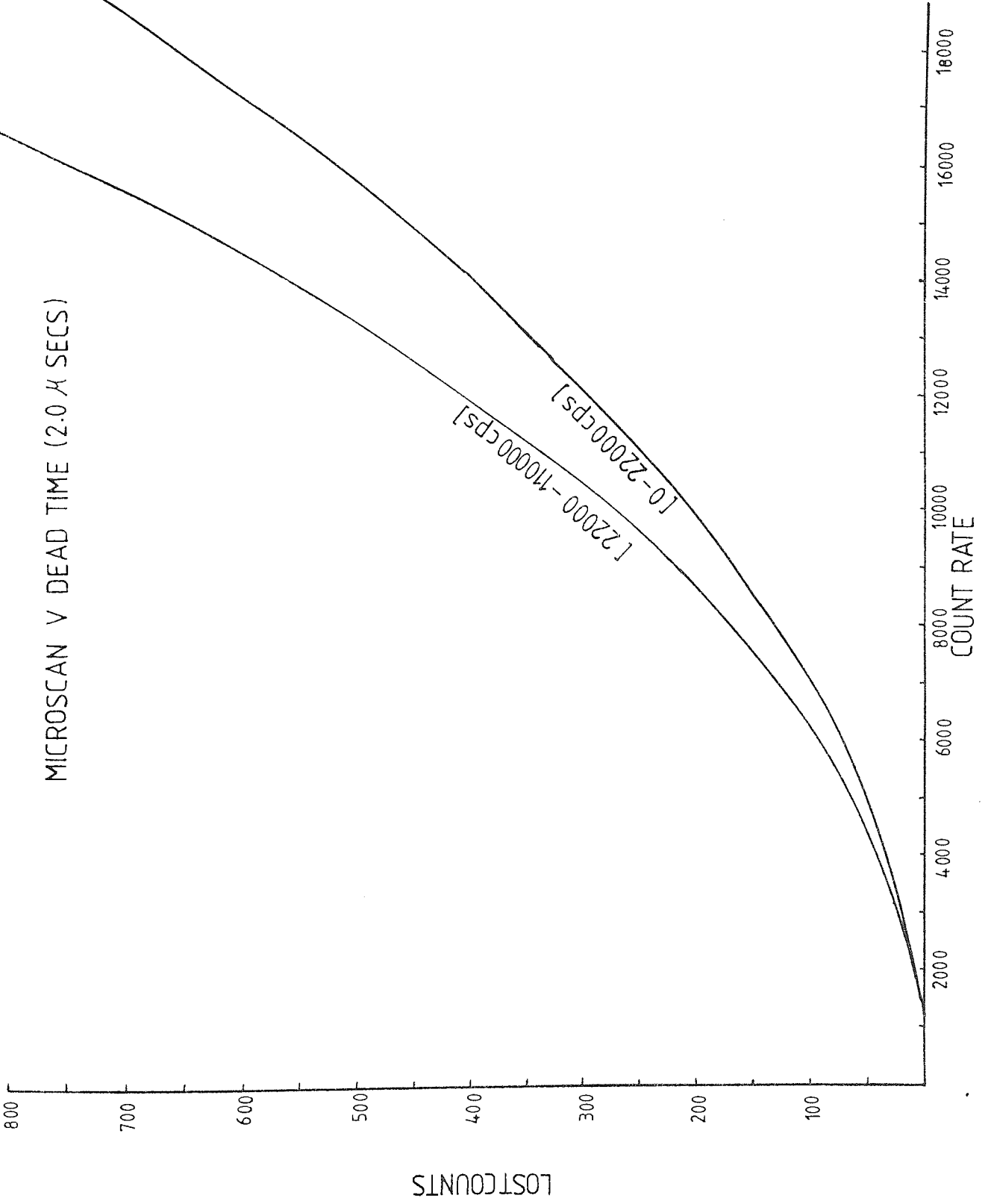
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