INTER RELATIONSHIPS BETWEEN SEDIMENTARY FACIES, DIAGENESIS AND FLUID FLOW IN THE GARVOCK GROUP, LOWER OLD RED SANDSTONE, SCOTLAND, U.K.

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DECLARATION

THE MATERIAL DESCRIBED HEREIN IS AS THE RESULT OF INDEPENDENT RESEARCH CARRRIED OUT AT THE DEPARTMENT OF GEOLOGY, GLASGOW UNIVERSITY, AND AT THE SCOTTISH UNIVERSITY REACTOR CENTRE, EAST KILBRIDE, DURING THE PERIOD OCTOBER 1985 TO MARCH 1989. ANY OTHER WORKS MENTIONED IN THIS THESIS HAVE BEEN DULY REFERENCED AND ACKNOWLEDGED

SIGNED

DEBORAH A KENNEDY

To Leslie,

- For everything !

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ABSTRACT

Sedimentary facies may be distinguished not only by their morphology and grain size but also by different diagenetic histories. In sand bodies which constitute hydrocarbon reservoirs, it is therefore of some interest to attempt to recognise and delineate these different diagenetic zones. A single sand bar within the fluvial succession of the Garvock Group Lower Devonian, was chosen for study, since this would aid in understanding the controls on the distribution of good reservoir characteristics to be found in association with fluvial sediments.

The Crossgates sediments showed a range of diagenetic zones which may reflect the diagenetic pathways defined by depositional environment, sand body geometry, and porosity / permeability anisotropy. The intrusion of a quartz tholeiite dyke during the Late Carboniferous has led to local hydrothermal overprints on the diagenetic history.

Porosity / permeabilty anisotropy within the Crossgates sequence can be closely correlated to the sedimentary facies observed within the sand bar. This porosity / permeability anisotropy has had a profound effect on the diagenesis of the Crossgates sequence.

Original differences in porosity and framework mineralogy have resulted in different diagenetic histories for different sedimetary facies. Within the sequence the upper regions of the bar were originally the finest-grained and more clay-rich, here porosity and permeability were poorer and fluid circulation more restricted, this has resulted in diagenetic effects being less marked. This contrasts with other locations where porosity and permeability may have been high and only subsequently reduced by compaction and diagenesis.

The diagenetic history can be briefly summarised as follows: Grain coating haematie and mixed layer clays are initially developed. Subsequent pore-filling kaolinite and associated minor quartz are prominent in the silty-grade facies. Calcite and contemporaneous anatase are pervasive, and partly replacive of earlier cements and detrital silicates, but are predominantly pore-filling. Pore-bridging fibrous illite is then developed and this is the final diagenetic event prior to dyke induced hydrothermal alteration. This hydrothermal alteration results in the devolpment of chlorite in sediments adjacent to the dyke, and the re-mobilisation of earlier carbonate cements.

Stable isotopic data indicate temperatures of precipitation for the carbonate of between 35

to 50^{o}C. The similarity of isotopic compositions within non-dyke affected sediments suggest a common origin for the carbonate. The data indicate that it is not one single source but a series of sources including contributions from overlying pedogenic carbonate sequences.

The presence of anatase and calcite as a diagenetic cements indicates enrichment in titanium, and (bi)carbonate. This indicates the possibilty of fluid circulation via convection occurring in the Garvock Group, with a net transport of titanium in pore water from the underlying Ochil Volcanic Formation.

The diagenetic history of the sediment sequence at Crossgates can be seen to be the result of the interaction of highly complex factors, which have both influenced and modified the diagenesis of the sediments. The implications from this study are that hydrocarbon reservoirs cannot be regarded as homogenous units, but as highly structured anisotropic bodies, whose horizontal and vertical anisotropies ultimately reflect depositional facies sand body geometry, fluid flow and diagenetic histories. Therefore the reservoir characteristics of such alluvial systems may be highly variable with resulting indications for oil and gas recovery.

CHAPTER ONE INTRODUCTION AND GEOLOGICAL SETTING

1.1 INTRODUCTION

The diversity of possible fluvial environments, associated with river systems, can lead to the lateral and vertical juxtapositioning of very different sediment facies, ranging from conglomerates and sands to silts and muds. Channel migration and vertical aggradation often lead to rapid, substantial lateral and vertical facies changes. Within this association, sediments may experience different pore water chemistries and fluxes and in certain environments, sediments may even be subject to seasonal evaporation.

Sedimentary facies are distinguishable not only by grain size and morphology but also, as a consequence of the above factors, by different diagenetic histories. Where fluvial sand bodies constitute hydrocarbon reservoirs, there may be in very close spatial association, related sediments of highly contrasted porosities and permeabilities. Such horizontal and vertical poroperm anisotropies reflect the influence of depositional facies, sand body geometry and fluid flow, and diagenetic histories. It is therefore of some interest to attempt to recognise and delineate these different diagenetic zones in a fluvial sand body. This would aid in understanding the controls on the distribution of good reservoir characteristics to be found in association with fluvial sediments. The recognition and mapping of such diagenetic zones within hydrocarbon reservoirs is important in defining the 'quality ' of that reservoir in terms of its production capability.

A single sand bar within the fluvial succession of the Lower Devonian Garvock Group, (Lower Old Red Sandstone (L. O. R. S.)), in the Crossgates area, Perth, Scotland (figure 1.1) was examined using a variety of techniques. It was chosen for study as it fufilled a variety of important criteria : The location, a road cutting, had only recently been exposed, so problems due to surface weathering and erosion were minimised.The unusually large scale of the structure allowed detailed sampling of the different component lithofacies which would permit diagenetic zones within the sediment body to be clearly recognised. The Crossgates sediments showed a range of diagenetic zones, which reflect the diagenetic pathways defined by depositional environment, sand body geometry, and porosity / permeability anisotropy. Intrusion of a quartz tholeiite dyke during the

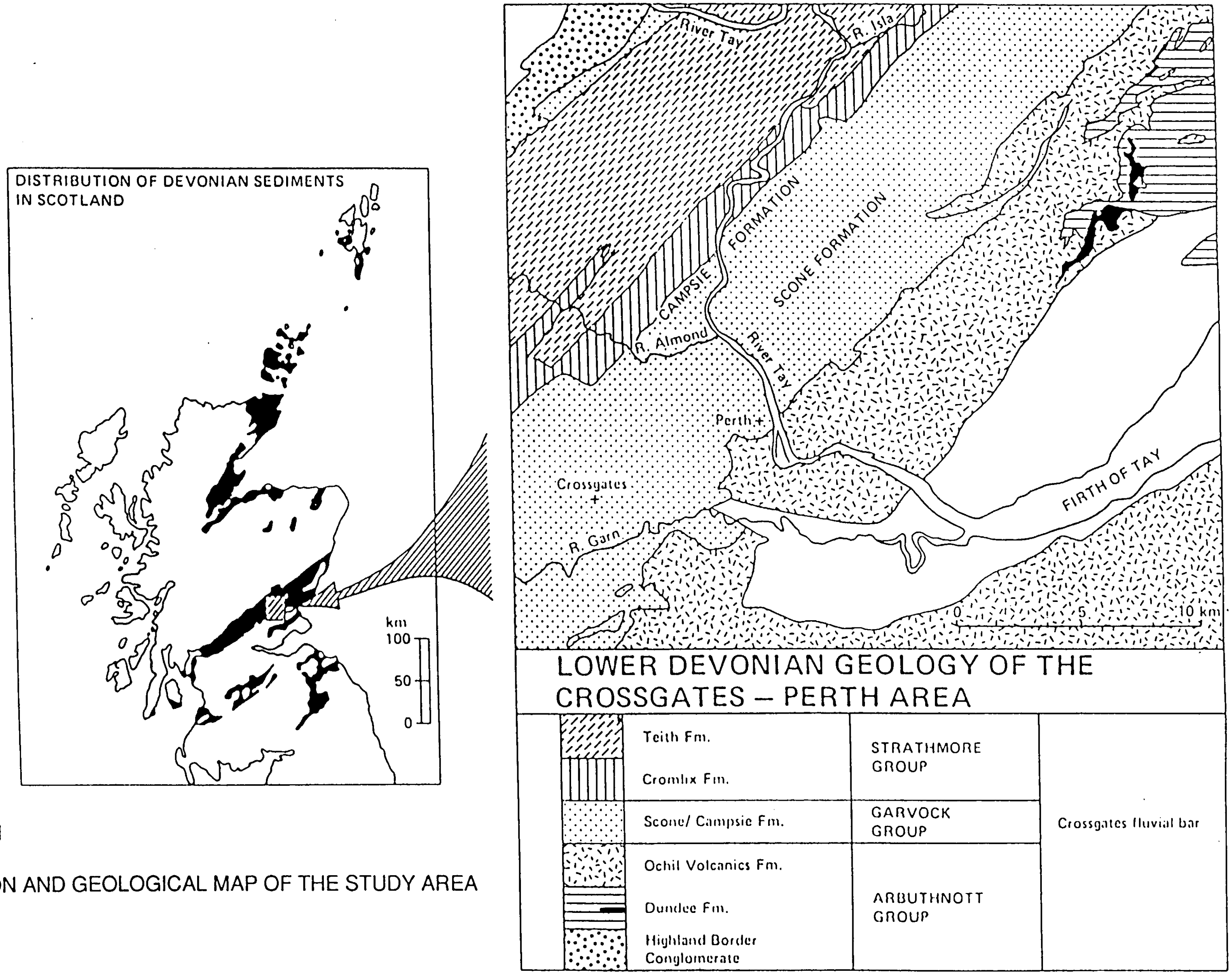


FIGURE 1.1

LOCATION AND GEOLOGICAL MAP OF THE STUDY AREA

Carboniferous (Stephanian) has led to local hydrothermal overprints on the diagenetic history and is of interest because of possible effects on the porosity and permeability.

Comparison of the framework mineralogies and the diagenetic assemblages, was accomplished using a variety of petrographic techniques, such as quantitative analysis (point counting), cathodoluminescence and S.E.M. studies with EDAX observations. This was complemented by quantitative results from electron microprobe analyses of the calcite cement in the sediments, X-ray diffraction analyses of clay fractions and stable isotope analyses of diagenetic mineral phases.

The data acquired offer some constraints on defining pore fluid chemistries and sources with respect to thermal and temporal evolution of the diagenetic cements during burial diagenesis and subsequent intrusion of the Carboniferous dyke. By studying the the distribution of such diagenetic zones in detail it may be possible to recognise zonation within a reservoir, and hence more accurately model the diagenetic features of that reservoir with the accompanying implications for oil / gas production and recovery.

1.2 GEOLOGICAL SETTING.

INTRODUCTION.

The studied sequence consists of continentally-deposited sandstones of Lower Devonian age which occur in the Midland Valley of Scotland. They are located within a large synclinal structure (Strathmore Syncline) which contains the most extensive outcrop of Lower Devonian strata in the Midland Valley.The history of the Midland Valley area prior to Devonian times is currently unclear. A number of hypotheses have been put forward relating the closure of the Iapetus Ocean during Silurian times (summarised in Anderton *et al.,* 1979), with northwestwards subduction in the area presently occupied by the Southern Uplands. Bluck (1984), also postulated that the pre-Devonian Midland Valley could have been a tripartite division of arc, proximal fore- arc basin, and marginal basin, subsequently juxtaposed by strike-slip and thrust faulting.

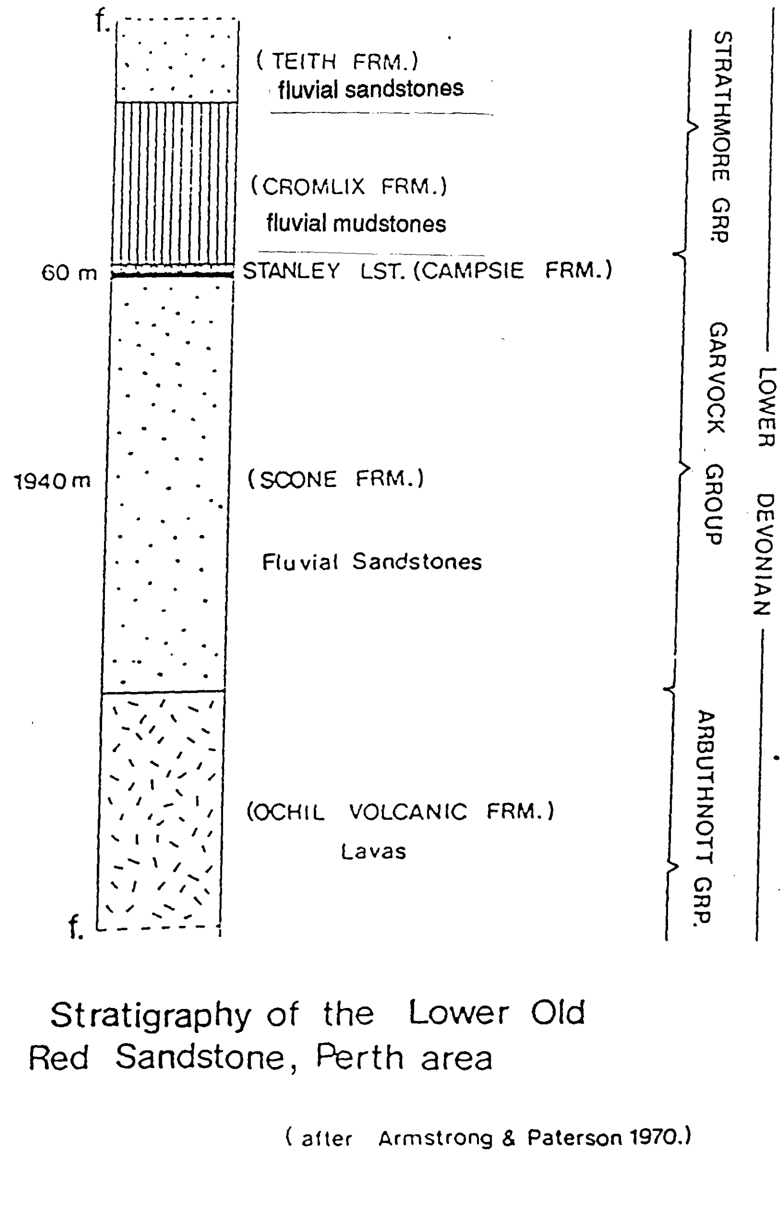
STRATIGRAPHY

The stratigraphical classification adopted for this study, is based on that of Campbell (1913) for the Lower Devonian sequence in Kincardineshire. This classification was further refined by Armstrong and Paterson, (1970). The general paucity of faunas and floras has resulted in the establishment of a broad litho-stratigraphy, the continuity of which is demonstrated by mapping. Therefore the Lower Devonian sequence in the Midland Valley has been subdivided into six litho-stratigraphical groups, commencing with the basal Dunnottar Group and ending with the Strathmore Group, (Table 1.1).

DEVONIAN.

Lower Devonian (Gedinnian - Emsian)

As indicated, the most extensive outcrop of Lower Devonian rocks in the Midland Valley occurs in the Strathmore region of Perthshire and Angus (Armstrong and Paterson, 1970). A thickness of over 9km. of strata is preserved in the axis of the northeast - southwest trending Strathmore Syncline, adjacent to the Highland Boundary Fault at Stonehaven. These strata thin to



Stratigraphy of the Lower Old Red Sandstone, Perth area

(after Armstrong & Paterson 1970.)

TABLE 1.1 STRATIGRAPHY OF THE LOWER OLD RED SANDSTONE, PERTH AREA the south towards Dundee and to the southwest towards the Firth of Clyde, where on Arran only 1.5 km. of strata is preserved. The Lower Devonian succession in the Strathmore Syncline dips steeply adjacent to the Highland Boundary Fault Complex (figure 1.2a) , suggesting a close possible association between basin growth and the development of the fault complex.

The sedimentary rocks of early Devonian age consist mainly of a series of often cross-bedded fluvial sandstones and conglomerates which are thought to have accumulated in a series of alluvial fan and plain systems, from sheet-flood, braided and low sinuosity streams. The channel-bar sand units are often grey and green, and may have very large cross-strata indicating deep channel systems. Associated with these, are thick siltstone-mudstone sequences which probably represent inter-channel areas. Mud clasts derived from overbank deposits are common, especially in the basal parts of channel units.

The Lower Devonian sediments are thought to have been deposited in two major basins lying within the Midland Valley, the Strathmore basin in the north and the Lanark basin in the south. Sediment accumulation may have been related to motion on fracture systems at the basin margins, which maintained upland areas on the basin flanks, as in both there is an element of lateral fill, but both basins are dominated by axial sedimentation which was deposited in rivers flowing towards the southwest.

Within the Strathmore area, palaeocurrent evidence (Armstrong *et al.*,1978; Bluck, 1978; Morton, 1979) from rocks of the Arbuthnott and Garvock Groups, suggests that the predominant direction of sediment transport occurred in a south westerly direction parallel to the basin axis (figure 1.2b),. It has been suggested that the Midland Valley fluvial system may have drained an area lying to the north- west of the present Scottish coastline during the deposition of the Arbuthnott and Garvock Groups (ie. Gedinnian-Siegennnian times).

During deposition of the sedimentary rocks of the Arbuthnott Group, thick andesitic lavas of the Ochil Volcanic Formation,were erupted onto the Early Devonian alluvial plains. These lavas may represent subduction- related volcanism associated with the northern margin of the closing Iapetus Ocean (Thirwall, 1981;1983).

The lavas of the Ochil Volcanic Formation contain quartzose sandstone / siltstone

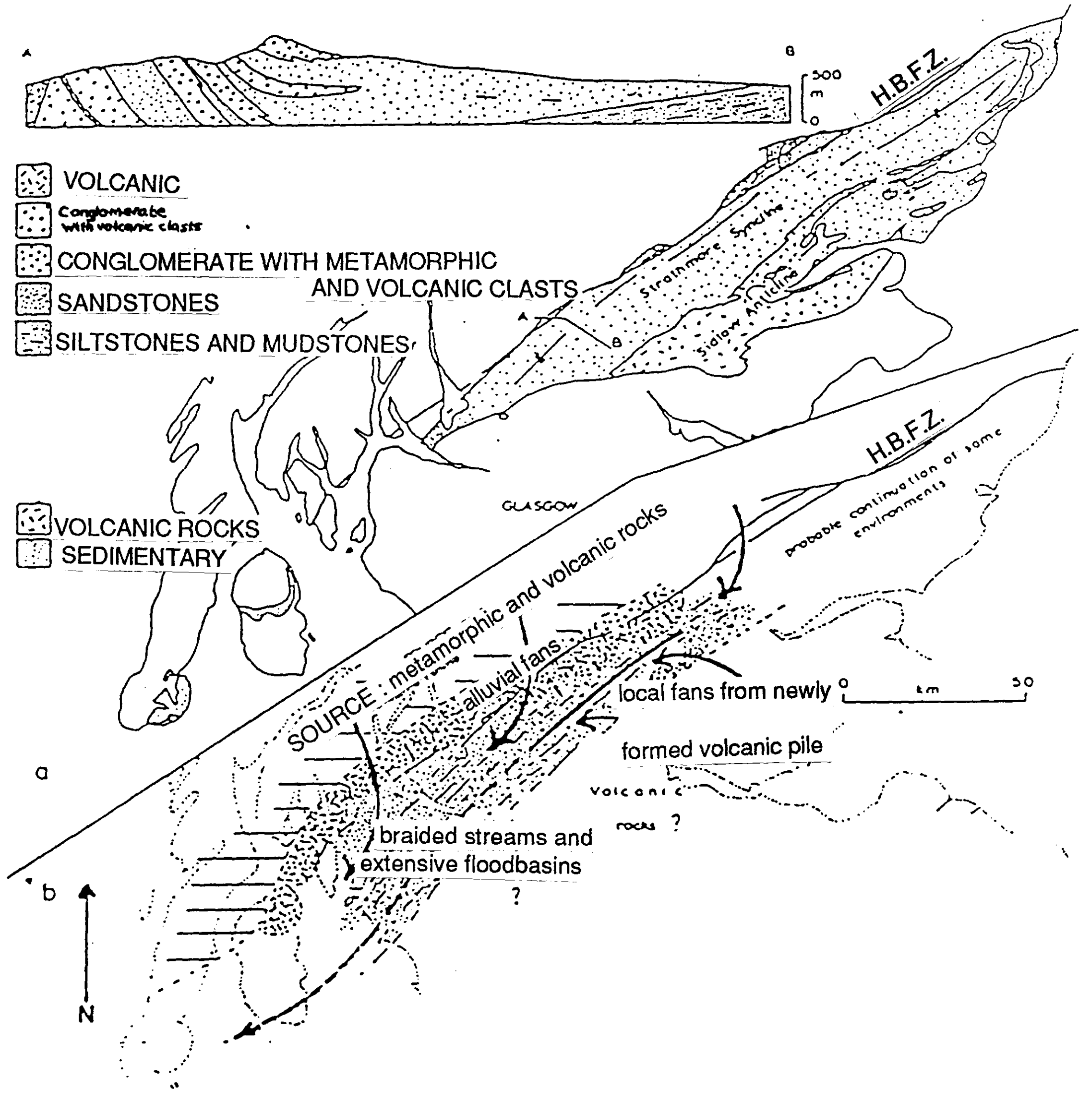


FIGURE 1.2a LOCATION AND CROSS SECTION OF THE STRATHMORE SYNCLINE

1.2b LOWER DEVONIAN PALAEOFLOW, MIDLAND VALLEY

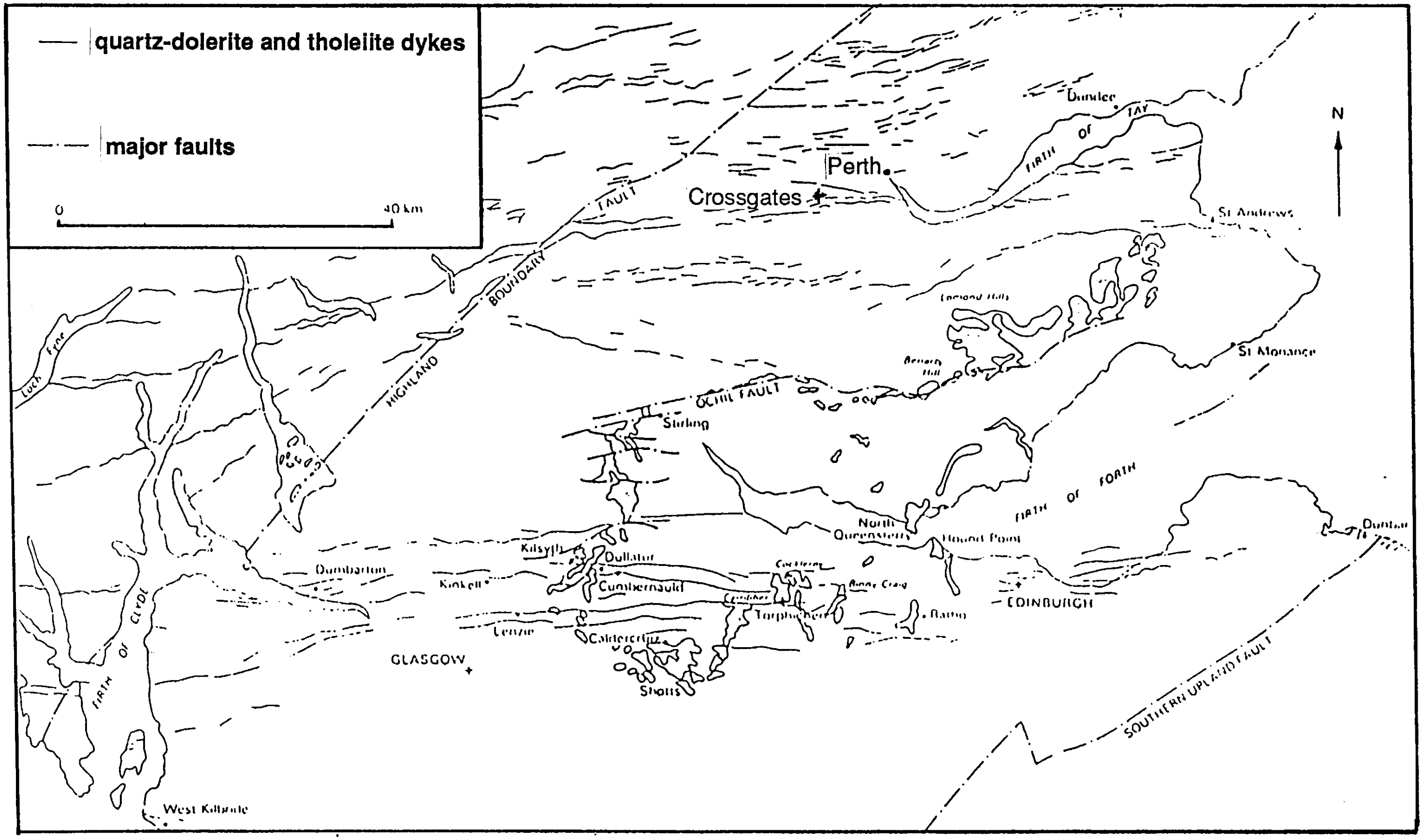
(Adapted from Bluck, 1978)

intercalations which suggest that the fluvial system was not wholly impeded by the eruption of the lavas. That the fluvial system was intermittently impeded is suggested by the lacustrine deposits of the Dundee Formation which occur as intercalations within the predominatly fluvial sediments of the group. Bluck (1980) suggests that the volcanic lava-piles may have divided the Early Devonian basin into two elongate basins running parallel to the axis of the main basin. This relationship is only poorly known, and may have only existed during deposition of the Garvock Group.

The rocks of the overlying Garvock Group, which include the Crossgates sequence, consist mainly of cross-bedded sandstone units which contain metamorphic and igneous clasts. Concretionary limestone detritus of intra-basinal origin also occurs and is thought to have formed probably as pedogenic carbonate within the mudstones of associated overbank deposits. The presence of these carbonates may reflect localised fluctuations of the water -table with periodic drying out of the flood-plains during which the carbonate concretions formed. The occurence of the concretionary beds and nodules of pedogenic carbonate (Stanley Limestone, Campsie Formation) near the top of the Garvock Group, are thought to indicate degeneration of the Early Devonian river system. This was accompanied by a change in climate towards more seasonal precipitation, with resultant fluctuations in the water-table and periodic drying out of the flood-plains allowing formation of the calcretes.

The rocks of the overlying Strathmore Group indicate a return to fluvial conditions, with the development of the mudstones of the Cromlix Formation. These mudstones outcrop on the southeast limb of the Strathmore Syncline, and pass laterally northwestwards into sandstones and conglomerates. These sedimentary sequences may represent the distal parts of an alluvial fan and plain system which lacked the southwesterly drainage pattern seen previously. Axial drainage is thought to have become re-established during the deposition of the upwardly-fining, cross-bedded sandstones of the Teith Formation which represent the uppermost unit of the Strathmore Group. However, in contrast to the rocks of the underlying Arbuthnott and Garvock Groups, the rocks of the Teith Formation suggest deposition by a meandering river system rather than the braided river system suggested by the underlying rocks.

Lower Old Red Sandstone sedimentation in the Midland Valley effectively ceased during



(After Cameron and Stephenson, eds., 1985)

FIGURE 1.3 LATE-CARBONIFEROUS QUARTZ-DOLERITE AND THOLEIITIC INTRUSIONS IN THE MIDLAND VALLEY late Siegennian or Emsian times (House et. al., 1977), coinciding with the onset of the tectonic activity which led to the development of the Strathmore Syncline and the associated Sidlaw Anticline. Southeastwards overthrusting occurred along the Highland Boundary Fault Complex which may reflect northwest- southeast crustal shortening. The peak of late Caledonian deformation in Scotland may therefore have occurred during late Early Devonian times, possibly synchronously with the Acadian Orogeny of Canada (Soper *et al.*, 1987).

The newly uplifted Lower Devonian rocks were subsequently strongly eroded and no rocks of Middle Devonian age have currently been described from the Midland Valley. Bluck (1980) has suggested that the NW Midland Valley may have developed as a sinistral strike- slip controlled extensional basin during Late Devonian times. This proposal has yet to be conclusively demonstrated.

CARBONIFEROUS.

Stephanian Intrusive Actvity.

The Lower Old Red Sandstone sediments at Crossgates were subsequently affected by volcanism during the Carboniferous. During the late Silesian (Stephanian), tectonism in the Midland Valley led to the intrusion of a suite of tholeiitic dykes along east-west extensional fractures (figure 1.3), one of which intruded into the Crossgates sediments. This swarm may possibly continue across the North Sea Basin and through the Oslo Graben; and may be related to extensional stress associated with lithospheric separation in a proto-North Atlantic rift (Rockall Trough) to the northwest of the British Isles (Russel and Smythe, 1980).

CHAPTER TWO SEDIMENTOLOGY OF THE CROSSGATES SAND BODY, GARVOCK GROUP.

2.1 SEDIMENTOLOGY AND FACIES STUDIED

The re - allignment of the A9 trunk road, at the Blackford bypass 3km. SW of Perth, led to the exposure of a large scale fluvial bar sequence at Crossgates (G.R. 048209), the road cutting itself exposes a single sand bar of approximately two km. in length.The sedimentary sequence at Crossgates is part of a series of stacked channel sands which occur in the immediate area. These sand bodies represent the sedimentary deposits of a major Lower Devonian SW-flowing fluvial system. The total areal extent of these bodies in the surrounding area is difficult to estimate due to the lack of exposure in the area. The sedimentary strata of the Garvock Group are only well exposed in road cuts in the area, although isolated outcrops and quarries are known. One borehole (Bogle Bridge, Perth, B.G.S.) is also known to penetrate the Group.

The study area satisfied a number of criteria for diagenetic examination. The road- cutting itself had been only recently exposed, so problems due to surface weathering and erosion were likely to be minimised, while the unusually large scale of the bar allowed detailed sampling of the various lithofacies which comprise the body, to be undertaken. This permitted characterisation of the body into distinct lithozones or lithofacies, followed by an attempt to model the diagenetic zones.

Modern sedimentolgical studies of large rivers, such as those of Fisk, (1944, 1947) and Coleman, (1969),on the Mississippi and Ganges Bramaputra, respectively, provide some guide for estimating the scale of these Lower Devonian river systems using present -day analogues. The minimum height of such sand bars in modern day analogues is between 2 and 3m., and this provides some impression of the scale of the river which deposited these Lower Devonian sand bodies. The minimum height of the Crossgates bar is approximately 13m. This represents the height of the body during the lowest flow stage of the river. During times of high flow, ie. during flood episodes, the bar may have been up to 20 m. deep indicated by field evidence. The width of the river itself is thought to have been in excess of 1km. *(B.J Bluck, pers. comm.)* . Morphologically, these bar deposits are lobate in form and occur within stream channels. Individual bar-forms may vary in size and form even within an individual river, and individual bars may sometimes coalesce together (figure 2.1). The characteristics of the sequence may vary according to the síze and depth of the channel. Typically, such fluvial deposits are reasonably well sorted, containing fining upwards medium to fine-grained sands with increased scale cross bedding. Sedimentologically, these deposits are thought to represent the products of mid channel bars, *(B.J. Bluck, pers. comm.)*. The Crossgates structure appears to represent an individual bar-form whichhad a minimum height of 13m. (low flow stage) and is at least 1km. in length from head to tail. The lobate structure is widest at the upstream end and narrows at the downstream end.

Lithologically, the upstream end of the bar, i.e. theBar-Head facies, normally contains the coarser-grained sediment. The sediment load can be seen to 'fine' downstream towards the Bar-Tail facies which consists at Crossgates of fine to medium-grained sandstones and siltstones. This flow stratification is clearly seen in the Crossgates sequence, and represents the progressive deposition of different fractions of the suspended bed load from head to tail. When the bars migrate downstream, the coarse bar-head and mid-bar facies migrate a little faster than those downstream. In this situation, the up-stream parts of the bar migrate over the downstream to produce a sequence of sediment which coarsens upward. Such a sequence is displayed on the southern wall of the road cutting at Crossgates, where vertically and partly laterally the bar-head, mid-bar and bar-tail facies are present. On the north wall of the road cut, and in fault contact with the bar sequence of the southern wall, occurs a sequence of overbank deposits. These comprise a highly varied lithological sequence which includes crevasse-splay and overbank deposits.

Using terminology modified from Bluck (1971), the Crossgates bar can be further divided sedimentologically into distinct regions or lithofacies, each with its own characteristic sedimentary assemblage. At Crossgates three main bar facies can be recognised in the field (figure 2.2) -

1. Bar-Tail
2. Mid-Bar

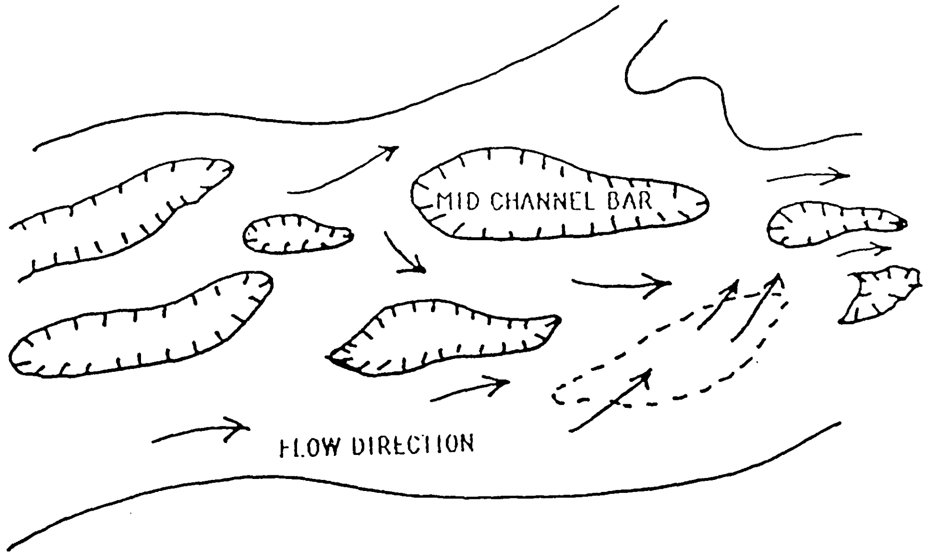


FIGURE 2.1 DISTRIBUTION OF MID- CHANNEL BARS WITHIN RIVER CHANNEL

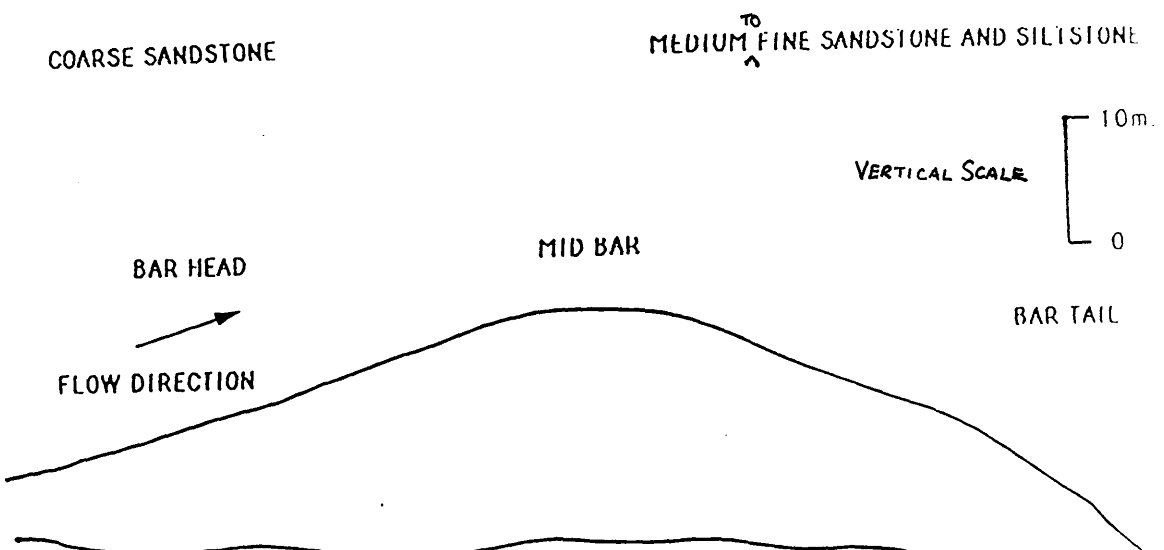


FIGURE 2.2 RE-CONSTRUCTED CROSSGATES BAR SHOWING DISTRIBUTION OF FACIES

3. Bar-Head

Associated with the main bar facies, Overbank and Crevasse Splay deposits also occur , and these represent the inter-channel areas, such as the flood-plain environment. The sediments of these lithofacies were also studied for comparison with the bar facies proper.

LITHOFACIES

At Crossgates, the basal channel floor deposit is partly exposed at several points. This Channel Floor Lag deposit consists of medium to coarse- grained sands and channel debris. These sediments, occasionally coarsen to a basal pebble deposit . This deposit provides the substrate on which the channel bar is built. The Channel Floor Lag deposit is not regarded as part of the true bar facies but indicates the base of the bar sequence.

BAR -TAIL.

Sediments within this facies, consist of well- sorted, fine to medium- grained angular, immature sub- arkoses. Occasional large scale cross - bedded units occur within the Bar-Tail facies, but otherwise the facies is characteristically massively bedded. The foresets are an alteration of fine sandstone-siltstone and medium-grained sandstone. Within individual bedding units, some micro-scale ripple laminations can be identified. These laminations are picked out by preferential alignment of phyllosilicate detritus, and it is thought that these represent an original sedimentary feature, with mica 'drapes' forming on ripple surfaces. Similar features can be recognised in modern sediments. This facies represents the downstream end of the bar structure (plate 2.1).

MID- BAR

Sandstones of this facies are fairly immature, but reasonably well- sorted. Trough Cross-strata predominate in this facies, and on a finer scale, some traces of remnant ripple drift can be seen in thin section. Sub- units within this facies can be identified and these fine upwards . However , the

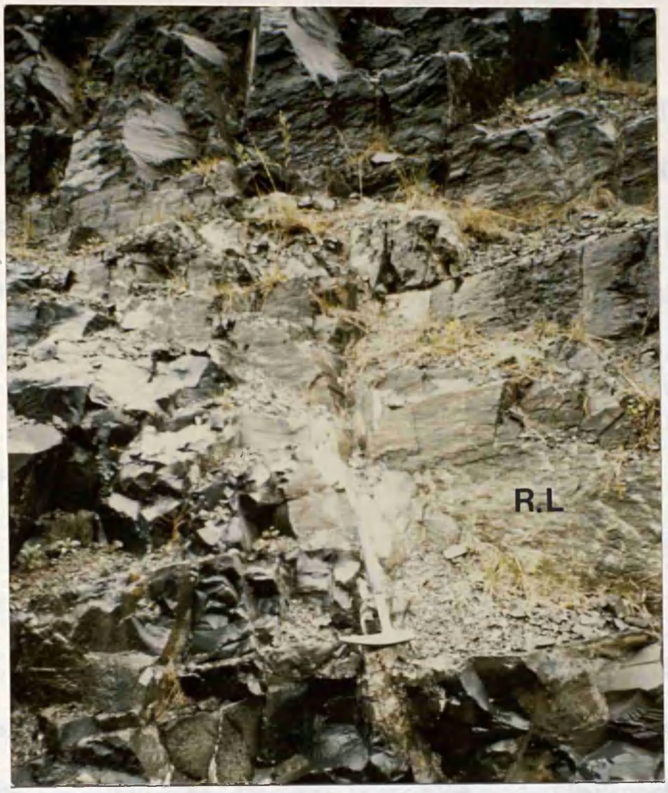


PLATE 2.1 TYPICAL BAR-TAIL FACIES

PLATE 2.2 TYPICAL MID-BAR FACIES

uppermost units of the bar are missing as a result of erosion. As the finer grade sands normally present within modern examples of this facies were not encountered. It is presumed that these have been lost due to erosional processes operating within the fluvial system. Approximately 7-8m. of sediment may have been removed, by erosion, based on estimates of the bar height to width ratio (plate 2.2).

BAR- HEAD.

Sedimentologically, this facies consists of cross-laminated bar sands comprising tabular planar cross bedded sands of diminishing amplitude (plate 2.3). The sediments consist of coarse sands, which noticeably fine upwards to a fine- grained, shale- bearing sandstone which shows evidence of occasional ripple drift. Shale pellets and rip -up clasts are common in this facies and were probably derived from the associated Crevasse Splay / Overbank deposits.

This fining- upwards sequence is also accompanied by a decrease in the scale of the sedimentary structures. Such a sequence is consistent with similar modern bar sequences, including that of the Brazos river in southeast Texas, (Bernard, *et al*; 1970) , where the presence of fining-upwards sequences in the sediments has been confirmed using geophysical logging techniques.

INTER-CHANNEL AREAS.

These are the fine-grained deposits which constitute part of the uppermost channel fill / flood-plain sequence. At Crossgates, two types of such sedimentary deposits, can be recognised i..e. crevasse splay and overbank sediments. (plate 2.4). These facies are in fault contact

Crevasse splays are channel margin deposits and occur when the natural river levees are breached during flooding episodes (figure 2.3). These gaps, or crevasses in the levees allow the river to flow through, depositing a lobate- or fan- shaped body of sediment known as a crevasse splay. Overbank deposits result from inundation of the flood - plain region during flooding and are deposited as thin sheets on the flood - plain surface.

Typically such deposits contain a high suspended sediment load. This sediment load,

PLATE 2.3 TYPICAL BAR-HEAD FACIES SHOWING TABULAR PLANAR CROSS BEDDED SANDS

PLATE 2.4 TYPICAL CREVASSE SPLAYS

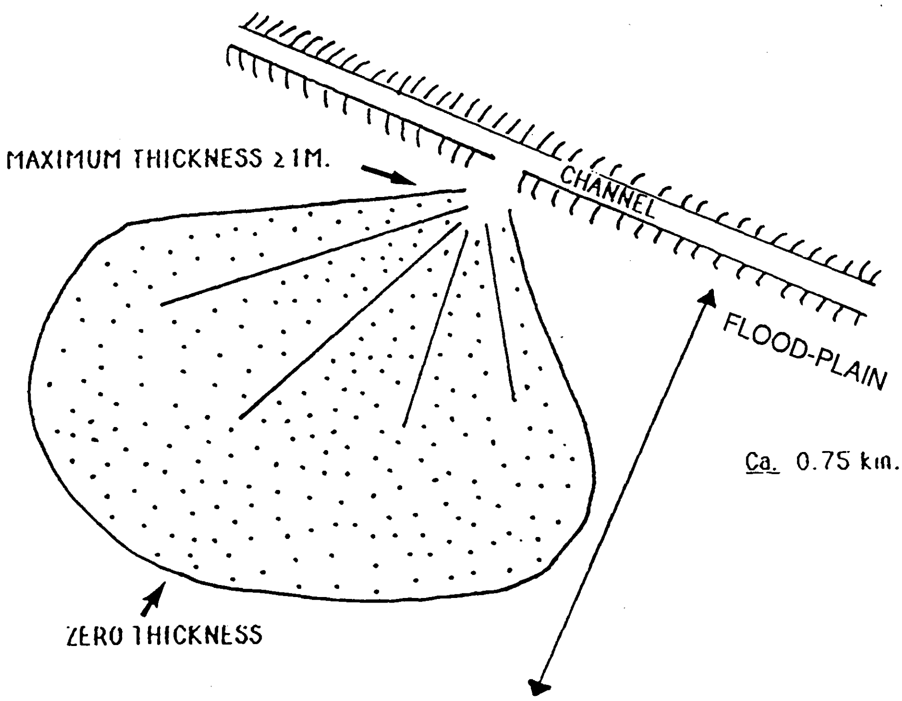


FIGURE 2.3 TYPICAL CREVASSE SPLAY / OVERBANK DEPOSITS OF THE INTER-CHANNEL AREAS

which consists of fine sand and silty clay, is deposited as a widespread thin blanket over the flood-plain. At Crossgates, these deposits consist of fine-grained argillaceous siltsones and mudstones, which are laminated, and ripple-marked. These deposits are commonly interbedded with sharp-sided and well defined sandstone units, which vary from a centimetre to a metre in thickness and appear as sandstone 'ribs' within the argillaceous deposits. The 'ribs' may represent the development of minor channels on the flood plain surface.

2.2 POROSITY AND PERMEABILITY ANISOTROPY

INTRODUCTION

Theoretical and observed porosity and permeability profiles for fluvial sand bars indicate the effects of hydraulic sorting on the grain size, detrital composition, and sedimentary texture of such sand bodies, and hence on the resultant diagenesis of such sequences. As a result of the above, the sand body can be recognised as having a series of varying porosity / permeability zones.

In well developed river- bars, the basal sands generally contain the coarsest sedimentary material and gradually fine upwards towards the top of the sequence (Stonecipher *et. al.*, 1984). Basal bar sands of this body are generally medium to coarse-grained, although occasionally a basal conglomerate or channel lag is developed. At Crossgates, this comprised a pebble conglomerate . However, this fining -upwards sequence is difficult to establish at a specific spatial point, since bars are not static features but undergo constant modification during their lifetime. Therefore, at some localities in a single bar the sedimentary sequence may appear to coarsen upwards, although the overall trend within the the whole of the body is to fine upwards. This results from the translation of the Bar- Head over the Bar-Tail as the sand body migrates downstream with time. Therefore care must be taken in reconstructing morphological relationships within such bar sequences.

Porosity and permeability anisotropy is developed due to the presence of distinct sub-facies within the bar, whose detrital mineralogies and, to a certain extent, the authigenic components, control and influence the porosity and permeability within the the bar as a whole.

BAR-TAIL

The porosity (as estimated from the amount of cement 'back-stripped' to give a ' minus - cement porosity ') is low or poor in this facies due to the presence of both diagenetic and detrital mixed layer clays. The facies is virtually sealed in terms of porosity. Although clay coatings occupy only a small volume of pore space, their development can restrict the diameter of pore throats. These grain- coats therefore provide effective permeability barriers within the facies and restrict the movement of fluids. This phenomenon is well known to occur in reservoir rocks and aquifers. Within this facies, the lack of diagenetic cements suggests that this may have been a 'restricted' system i.e 'restricted' to the passage of pore fluids. Clay mineral coatings also coat detrital (chemically unstable) grains and, by prophylactic action, prevent their dissolution and contribution of solutes to pore fluids.

MID- BAR

Increasing original porosity and permeabilty occurs in this facies due to the coarser nature of the original sediments . This allowed some circulation of pore fluids to occur, despite the pore space not being particularly well- interconnected. The result is that diagenetic effects are more evident than in the Bar-Tail (See chapter three).

BAR- HEAD

Primary porosity and permeability in this facies after depositon was high with porosity of up to a maximum of 30% being visually estimated in some samples. The clay content of the samples is low, with both detrital and diagenetic clays being almost wholly absent. The pore space is comprised of large open pores which are well connected. Within this facies, pore fluids appear to have been able to circulate through the sands, with little in the way of restrictions as to their movementas witnessed by the deposition of pore water derived cements. The result however, is that the final porosity and permeability, or poroperm, in the "clean" sands can be less favourable as reservoir characteristics than for "dirty " sands due to the occlusion of pore-space by pore water cements. Blackbourn, (1984) observed this relationship in a comparison of finer grained "dirty " " Ness " sands with coarser " cleaner " " Etive " sandstones.

CREVASSE SPLAY / OVERBANK SEDIMENTS

The sediments of this flood- plain area typically show marked low or poor porosity and permeability. This is due to the argillaceous nature of the original deposits. Any original porosity has been subsequently infilled by authigenic mixed layer clays and haematite.

SUMMARY

The sand body as a whole shows zones of distinct porosity / permeability anisotropy. This porosity /permeability anisotropy has a profound effect on the diagenesis of the sedimentary body and can be classed as one of the major influences on the subsequent diagenetic history of the sequence. The anisotropy observed within the sequence can be closely correlated to the sedimentary facies within the sand body and, as such, most likely arises from the effects of hydraulic sorting on the grain size, detrital compositon and sedimentary texture of such sand bodies (figure 2.4).

FACIES	TEXTURE		POROSITY	PERMEABILITY
	GRAIN SIZE	SORTING		
BAR TAIL	Fine to medium	Well sorted	Poor; very fine pores	Low
MID BAR	Sub units fine upwards	Reasonably well sorted	Intermediate; pores not well interconnected	Intermediate
BAR HEAD	Coarse	Intermed.-poor	Good; pores well connected	High
C.S / OV.	Fine	Well sorted	Poor; extremely fine pores	Low

FIGURE 2.4 POROSITY-PERMEABILITY RELATIONSHIPS WITHIN THE CROSSGATES SEDIMENTARY FACIES

2.3 PETROGRAPHY OF THE GARVOCK GROUP IN THE CROSSGATES AREA.

INTRODUCTION.

The overall petrography of the sediments, which comprise the bar was studied using a number of petrological and geochemical techniques including X-ray Diffraction. Approximately 40 thin sections and accompanying rock samples were examined . These thin sections were examined using a standard polarizing petrological microscope. Some thin sections were stained with Alizarin Red-S and potassium ferricyanide to test for the presence of dolomitic and ankeritic cements. The staining was accomplished using the method outlined by Dickson, (1966). All thin sections were quantitatively described using a Swift digital point -counter, with a total point - count of 1000 counts per section. Point count data are presented in Appendix 3.

Textural relationships, detrital and authigenic morphologies were examined using an electron microscope equipped with an energy dispersive analysis of X-rays (EDAX) system. This technique was useful in the recognition of clay minerals whose S.E.M. morphologies were similar; and in the identification of other authigenic phases including anatase and goethite. Cathodoluminescence was used to examine the pervasive carbonate cement, and resulted in the recognition of this as a singlegeneration cement. Identification of the clay minerals was accomplished using standard X-ray diffractometer (X.R.D.) techniques. An electron microprobe was used to examine for possible compositional variations within the carbonate cement.

DETRITAL MINERALOGY

The studied samples overall are sub-angular, fine to medium-grained sandstones and approximate, using Folk's, (1968) classification scheme to sub-arkoses and arkoses (figures 2.5 a,b,c,d). Within the bar lithofacies themselves, siltstones occur in both the Bar-Tail region, and in the flood-plain sediments (Crevasse Splay and Overbank deposits) where they predominate. These Inter -channel siltstones are also more micaceous and contain lesser amounts of quartz and feldspar than those of the bar facies proper. The majority of the detrital grains were mono- and polycrystalline quartz. These two quartz types were not differentiated in the point - count data.The remainder of the grains consist of detrital feldspars, biotite, some chlorite and rock fragments. Heavy

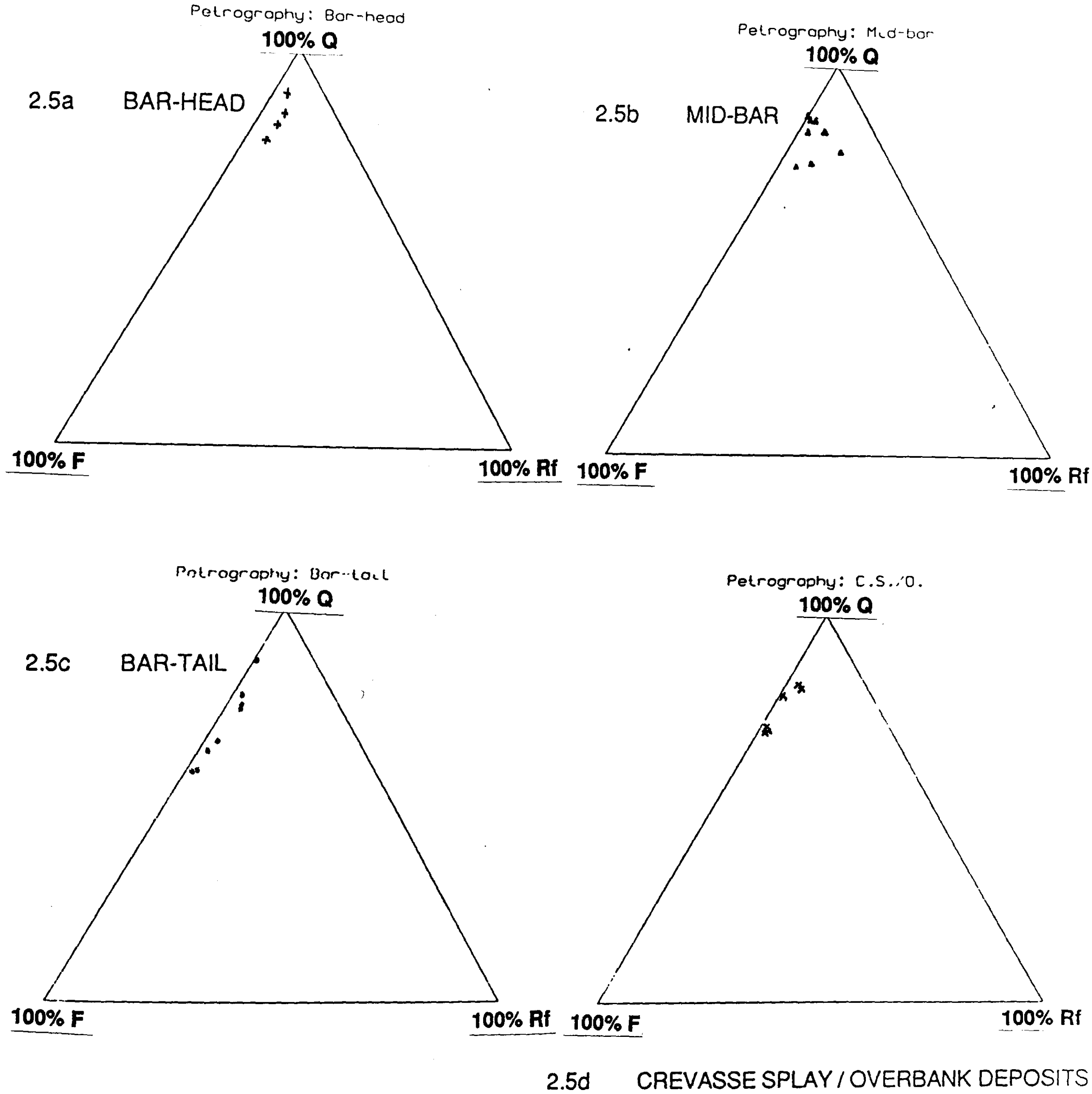


FIGURE 2.5 Q-R-F DIAGRAMS FOR THE CROSSGATES SEDIMENTS

minerals were also present, and include rutile and corroded garnets.

QUARTZ

Quartz was the most abundant detrital component of these rocks. Both monocrystaline and polycrystalline quartz grains occur, although the monocrystalline was the most abundant variety. Polycrystalline quartz was present in lesser amounts and this polycrystalline quartz was probably derived from a metamorphic provenance. The mineral grains were sub-angular and most were strongly embayed due to dissolution by later pore fluids (plate 3.19). Some grains showed euhedral terminations which are thought to be associated with diagenetic outgrowths (refer to section 3.4 - 'quartz').

FELDSPAR

Both plagioclase and orthoclase feldspar were present within the samples. The feldspars are present in both altered and unaltered states. Untwinned orthoclase feldspar is the most abundant feldspathic component in these rocks. Microcline and plagioclase are less abundant. Alteration and dissolution of the feldspars is common, this alteration commonly taking the form of the development of sericitic mica (plate 3.12). However ,since both 'fresh' and altered feldspars are present in the same sample, some of this alteration may be pre - depositional. The feldspar grains may also have been derived from different sources, each of which had undergone differing degrees of weathering.

MICA

Both biotite and muscovite were present in the rock. Most of the detrital phyllosilicates show evidence of alteration. Expansion and splaying of the grain terminations is common (plate 2.5). This results from the formation of diagenetic haematite as Fe is expelled from the biotites. 'Ghosting ' of the micas is also seen in the form of the pseudomorphing by haematite (plate 3.4). Unaltered micas also occur and are present as elongate grains which often show little evidence of later compaction.

PLATE 2.5 S.E.M. PHOTOGRAPH OF ALTERED BIOTITES SHOWING START OF EXPANSION AND SPLAYING OF THE GRAIN TERMINATION (P 1.)

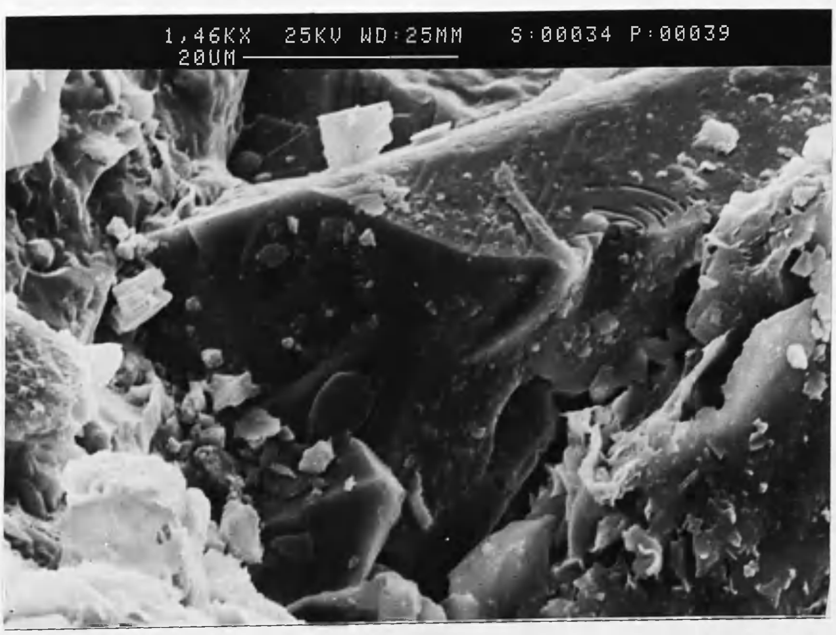


PLATE 2.6 S.E.M. PHOTOGRAPH OF DETRITAL GARNET, SHOWING CORROSION DAMAGE. IDENTIFICATION OF GARNET CONFIRMED BY EDAX ANALYSIS (P 20.)

LITHIC FRAGMENTS

Lithic fragments constitute only a small proportion of the detrital mineralogy of these samples, i.e. < 5% on average. Sedimentary, metamorphic and igneous clasts were all observed within the samples. Metamorphic clasts were predominately of schist and quartzite. Clasts of sedimentary origin were represented by the pres ence of chert fragments, rip-up clast and shale pellets. Volcanic fragments are the most abundant lithic fragments, with rhyolitic clasts predominating. The lithic clasts show a high degree of rounding which would be consistent with a high degree of transport and/or a multi-cycle origin. Alteration of the clasts is common and many grains show partial to complete dissolution.

Rip- up clasts and shale pellets are common, but are probably locally sourced being derived from associated flood plain sediments, and therefore not transported any significant distance as they show little degree of rounding.

HEAVY MINERALS

The heavy mineral component of the samples includes ziron, rutile, corroded garnets and occasionaly tourmaline. Allof the above are only present in trace amounts in these sediments, with garnet being the most abundant heavy mineral. Corrosion of the garnets appears to have taken place prior to incorporation in the sediment (plate 2.6). These heavy minerals have most likely been derived from a pre-existing sandstone, and are reworked since they most likely derive from metamorphic and igneous sources.

OPAQUE MINERALS

Detrital iron oxides were present in small amounts in these rocks and are thought to result from the incorporation of sediment derived from the weathering of a pre-existing reddened source.

TEXTURE

Textural relationships within the bar facies are related to the environment of deposition. In general, the samples are sub-angular to angular, fine to medium-grained sandstones. The degree of sorting is variable and can range from quite well- sorted to well-sorted, depending on the facies.

Within the thin sections, distinct ripple laminae can be picked out by 'mica drapes' and it is assumed that this is an original sedimentary feature formed during sediment deposition. The apparent lack of rounding in many of the detrital grains probably reflects a significant lack of sediment transport and possibly also the environment of deposition.

The Garvock Group sandstones in this area appear to have undergone only a small degree of compaction prior to cementation. This is indicated by the lack of sutured grain contacts and the presence of relatively undeformed phyllosilicates. In some samples, undeformed micas are orientated at 90° to each other (plate 3.17), indicating that compaction was not a significant event prior to cementation.

Another line of evidence for a low degree of compaction is the presence of undeformed primary pore space (now cemented), which retains the original pore geometry and shows no distortion due to compaction (plate 3.14). Therefore, it is unlikely that mechanical compaction significantly affected the porosity prior to cementation. This indicates that the original porosity approximates to that measured today, (20-25% on average in the most porous regions, ie. the Bar -Head facies). These porosity measurements represent minus -cement porosities, ie the void space left after the removal of the cement . Such evidence indicates that in the more porous regions of the bar, porosity may originally have been quite good with large areas of void space. The later reduction in porosity was therefore more probably a function of cementation , rather than due to mechanical compaction.

SUMMARY

The samples studied were mainly sub-angular to angular, fine to medium-grained sandstones. Siltstones occur in the deposits of the Bar-Tail facies (figure 2.5 c) and predominate in the Crevasse Splay and Overbank facies (figure 2.5d). The siltstones are more micaceous than the sandstones and contain lesser amounts of quartz and feldspar than the more coarse facies of the Bar -Head. Both monocrystalline and polycrystalline quartz occur as detrital grains, but were not differentiated in the quantitative descriptions. These quartz grains comprised the majority of the detrital grains. The remainder consist of detrital feldspars, biotite, some chlorite and rock fragments, i.e. mainly igneous and metamorphic clasts. Heavy minerals were also present and included rutile, rare tourmaline, and corroded garnets.

CHAPTER THREE DIAGENESIS OF THE GARVOCK GROUP SEDIMENTS, CROSSGATES.

INTRODUCTION

Original differences in porosity and framework mineralogy have resulted in different diagenetic histories for the different facies. Since the upper regions of the sequence were originally finer grained and more clay-rich than other parts of the sequence, original porosity and permeability were poorer. Fluid circulation during burial was therefore more restricted and the diagenetic effects less marked. This contrasts with the lower parts of the bar where porosity and permeability may have been high originally and only subsequently reduced by compaction and diagenesis. The diagenetic sequence for the sediments is outlined below :-

3.1 HAEMATITE.

i). DETRITAL HAEMATITE.

It is extremely difficult, using current petrographic techniques, to establish whether or not any of the haematite present in the samples results from the weathering of a pre-existing reddened source. The presence of haematite 'leaves' (indicating complete replacement of detrital phyllosilicate grains) in intimate association with 'fresh' biotites may indicate the reworking of partially or completely oxidised detritus. Friend *et al.* (1963) notes this feature on Arran and Friend (1966) suggests that the Devonian sediments of the Catskill Mountains could represent the mixing of detritus which had undergone different degrees of weathering. It is therefore reasonable to suggest that both authigenic and detrital haematite are present within the sample.

ii). POST-DEPOSITIONAL AUTHIGENIC HAEMATITE.

The presence of grain to grain contacts which lack haematite grain- coats indicates that at least some of the haematite was formed post-depositionally. Glennie (1970) has also observed similar haematite-free grain boundaries within aeolian sandstones and has suggested a post-depositional origin for these fine particulate grain- coating haematites . Walker (1967) has suggested that the post-depositonal formation of haematite may have occured in alluvial fan and tidal flat sediments of the western U.S.A. Here, diagenetic *in-situ* reddening of sediments of Pliocene to Recent age occurs, although it is extremely slow acting.

Turner (1974) suggests diagenetic haematite formation as the mechanism for the formation of haematite in Silurian sandstones in southern Norway.The process is thought to involve both the weathering of pre-depositional iron minerals, followed by *in-situ* breakdown of detrital phyllosilicates namely biotite, to give mixed-layer clays and immature iron hydroxides. These are then introduced into the sediment as amorphous iron hydroxide and iron-bearing clays.

The red colouration seen in sediments is due to the red ferric oxide pigment in haematite (α -Fe_2O_3). This is most likely formed during oxidation of iron hydroxides and the diagenetic breakdown of Fe-silicates and detrital iron-bearing clays. Walker (1967) suggests a possible reaction for the transformation of amorphous limonite to goethite and finally to haematite e.g.

$$2Fe(OH)_3 \rightleftharpoons 2HFeO_2 + 2H O_2 \rightleftharpoons Fe_2 O_3 + 3H_2 O$$

The oxidation of these Fe-hydroxides is aided by elevated temperatures, although the main requirement is high sustained ground- water flow provided by rainfall and runoff. Such conditions probably existed during Lower Devonian times. Jawad Ali and Braithwaite (1977) regard the mineral assemblages of the Strathmore, Garvock and Arbuthnott Groups as being not fully oxidised, and suggest that this may be the result of an incomplete weathering cycle which was terminated by events at the end of the Lower Devonian.

With reference to the various sub-facies of the the sand bar, muds and silts rich in iron hydroxides and detrital iron rich clays would be preferentially deposited in the finer grained regions of the bar e.g. the Bar Tail, as well as within the Crevasse Splay / Overbank deposits. The flood-plain areas were mostly above the water-table where oxidising conditions would prevail, and it is in sediments deposited in this environment that Fe oxides are most strongly developed. Both authigenic haematite and goethite occur in these facies

Typically, within these Crossgates sediments, the haematite is found in the form of grain coats and 'leaves' of haematite pseudomorphing after biotite (plate 3.1). Biotite is the only abundant silicate mineral with a significant iron content, which occurs within the channel sands of the Scone Formation channel sands. No pyroxenes or hornblendes have been identified from thin section. There is however no way of knowing whether or not other iron silicates were present at the time of depositon. Such components may well have been present, since Walker (1967) records a 60% loss of hornblende by interstitial alteration in sediments of Pliocene age in Baja, California.

The biotites show a variety of diagenetic replacement textures. These vary from completely 'fresh' grains to almost totally replaced grains, now pseudomorphed by haematite (plate 3.2). Such features have previously been recognised in rocks of the Lower Old Red Sandstone (Lower Devonian) in Scotland by Turner (1975) and in the Ringerike Group (Silurian) of southern Norway (Turner, 1974).

Characteristic stages in the alteration of the phyllosilicates include the initial reddening of cleavage surfaces and grain margins, followed by the development of opaque haematite along cleavage surfaces (plate 3.3). In some cases, biotite has almost been totally replaced by haematite and these pseudomorphs can be recognised as such because they preserve the grain shape of the original phyllosilicate, i.e retain the 'leaf'- like phyllosilicate form (plate 3.4).

In some biotite grains, a post-depositional origin for some of the haematite is further supported by the preservation of cleavages which show distortion due to compaction, similar to that seen in some of the unaltered grains. The final stages of haematite formation were therefore undoubtedly post- depositional.

iii). DISRUPTION OF GRAIN- COATS.

Post- dating the diagenetic events which led to the eventual formation of haematite, the influx of later CO_2 - rich pore- waters led to the disruption of the earlier grain-coats. Haematite can now be seen to be incorporated into areas of calcite cement, particularily in those regions of the bar which were preferentially enriched in haematite.

Under the S.E.M., haematite occurs as rounded or hexagonal-shaped crystals or platelets which are randomly orientated and commonly intersect each other. The diameter of the platelets is

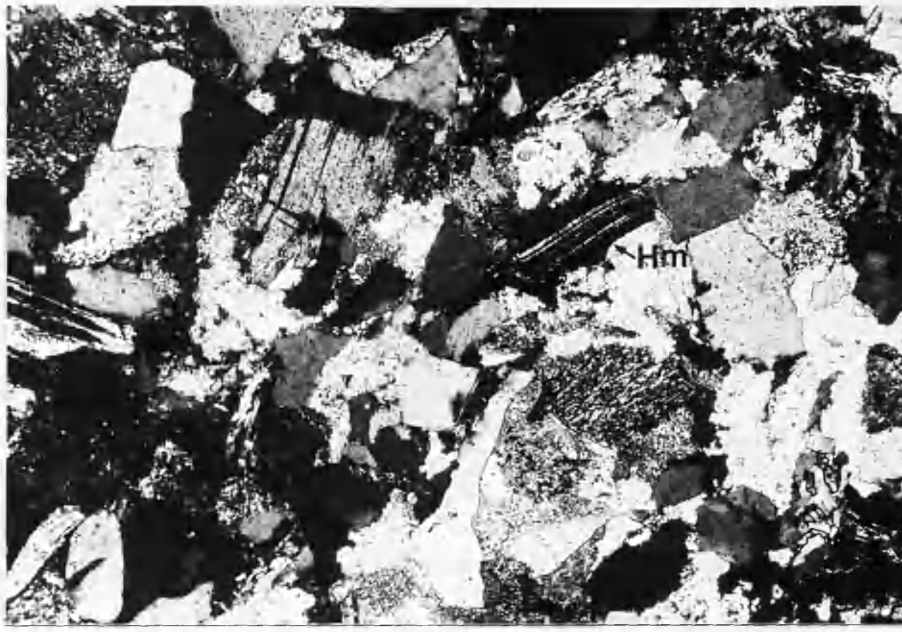


PLATE 3.1 PHOTOMICROGRAPH OF PSEUDOMORPHING HAEMATITE (Hm) AFTER BIOTITE (P 16.) (X 40)

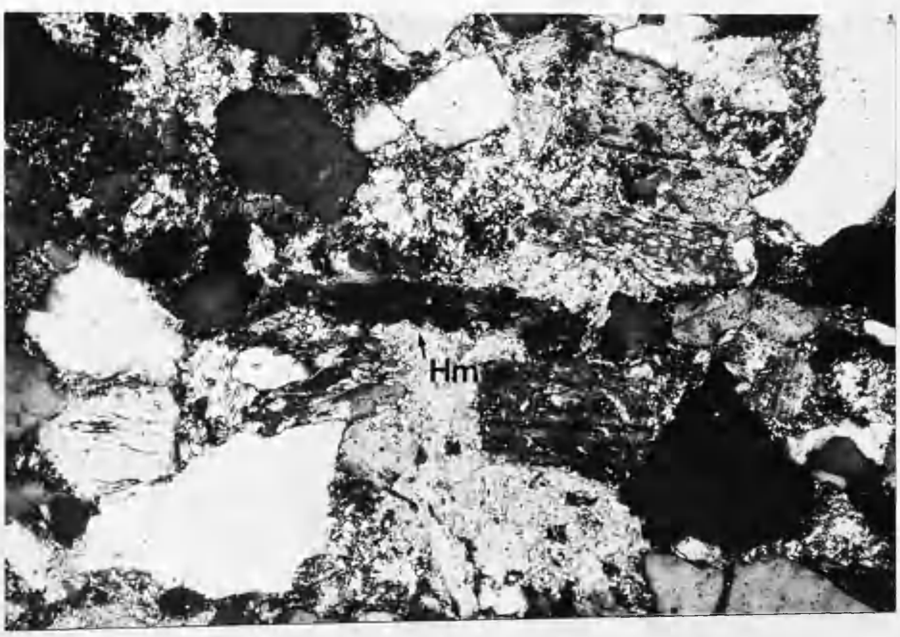


PLATE 3.2 PHOTOMICROGRAPH OF DETRITAL BIOTITE ALMOST TOTALLY REPLACED BY HAEMATITE (Hm) (P 3.) (X 80)

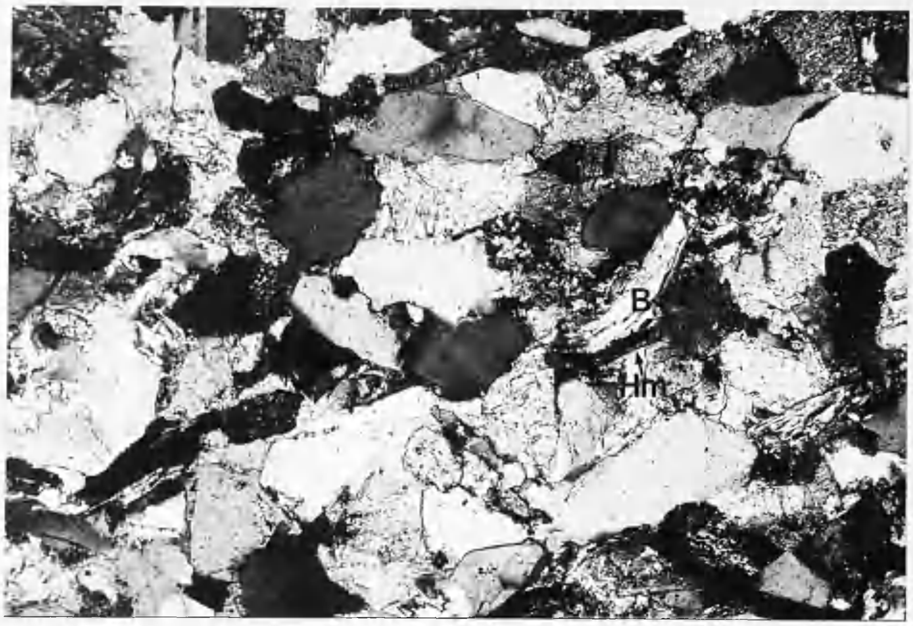


PLATE 3.3 PHOTOMICROGRAPH SHOWING DEVELOPMENT OF OPAQUE HAEMATITE (Hm) ALONG CLEAVAGE SURFACES OF BIOTITE GRAIN (P 13.) (X 40)

PLATE 3.4 PHOTOMICROGRAPH SHOWING 'GHOSTING' OF BIOTITE DUE TO REPLACEMENT OF AUTHIGENIC HAEMATITE (P 11.) (X 40)

approximately 5 μm and individual plates may be 1 μm in thickness (plate 3.5).

iv). SUMMARY

In summary, the haematite within these sediments is the result of both authigenic *in-situ* formation and incorporation of detrital haematite. This detrital haematite is most probably derived from the weathering and erosion of other red- bed units in the sediment source area. Authigenic goethite is also present which probably formed as an intermediary step to the development of haematite. Haematite and goethite are preferentially concentrated into the Bar-Tail and Overbank / Crevasse Splay sediments. Conditions in these two facieswere more suitable for their formation than in the other coarser-grained bar facies which have lower concentrations of iron hydroxides and iron-bearing detrital clays (Table 3.1).

Within the studied samples, authigenically-formed haematite appears to be predominate over that of detrital origin. It is assumed that most of the haematite seen is the result of diagenetic formation. The lack of overall reddening in the Garvock Group of the Lower Devonian is thought to be due to incomplete oxidation of the sedimentary sequence resulting from an incomplete weathering cycle.

3.2 MIXED- LAYER CLAYS

Mixed- layer clays are indicated by XRD analyses (figure 3.1) to be present within the sediment samples. In thin section, two clay morphologies are observed. The clay occuring as both grain coats and pelicles and also as larger aggregate patches frequently infilling the pore space. Under the S.E.M., these clays can be seen to form sheets with lath-like projections, exhibiting characteristics of both Illite and smectite, with both lath and cellular stuctures. Since mixed-layer clays are composed of more than one clay type, the composition and morphology of these components can be highly variable (plate 3.6).

The former mophology of pore-lining clays is thought to represent the development of early authigenic mixed- layer illite-smectite clays. This was probably associated with the development of iron oxides during the formation of haematite. Both the iron oxides and the mixed-layer clays

PLATE 3.5 S.E.M. PHOTOGRAPH OF AUTHIGENIC HAEMATITE (H) PLATELETS (P 17.)

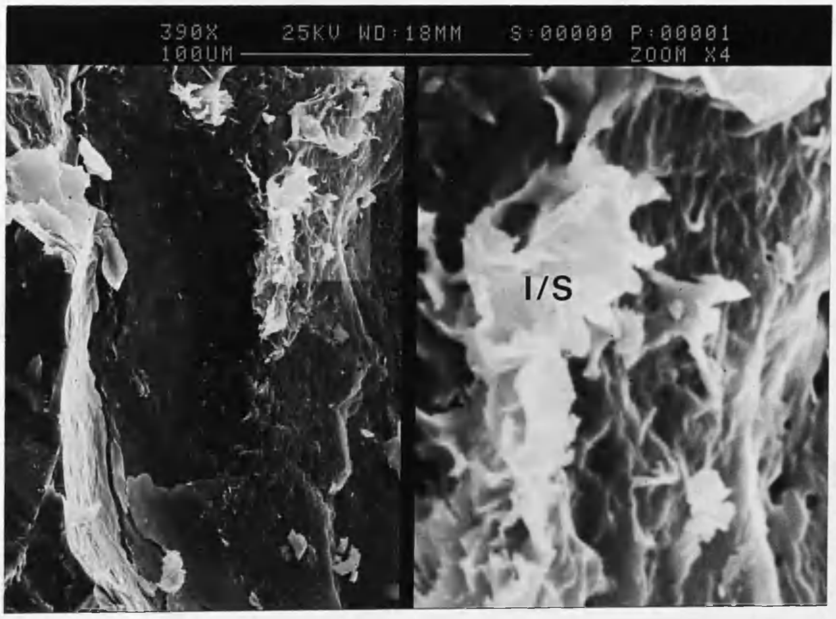
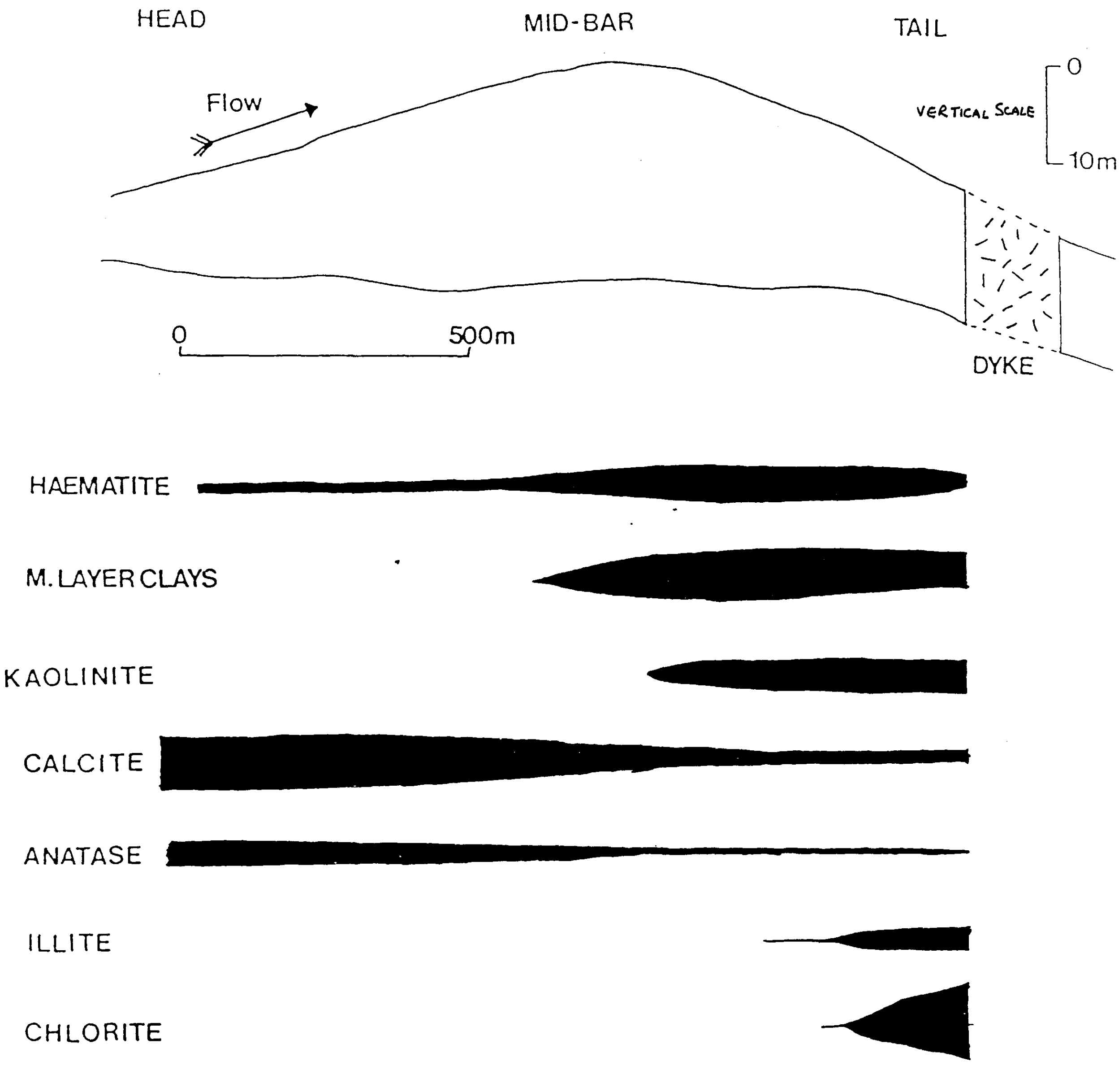


PLATE 3.6 S.E.M. PHOTOGRAPH OF MIXED-LAYER ILLITE / SMECTITE (I / S) WHICH EXHIBITS VARIABLE MORPHOLOGY WITH BOTH LATH AND CELLUAR STRUCTURES PRESENT (P 4.)



Variation of cement within the Bar facies

TABLE 3.1 VARIATION OF CEMENT WITHIN THE BAR FACIES

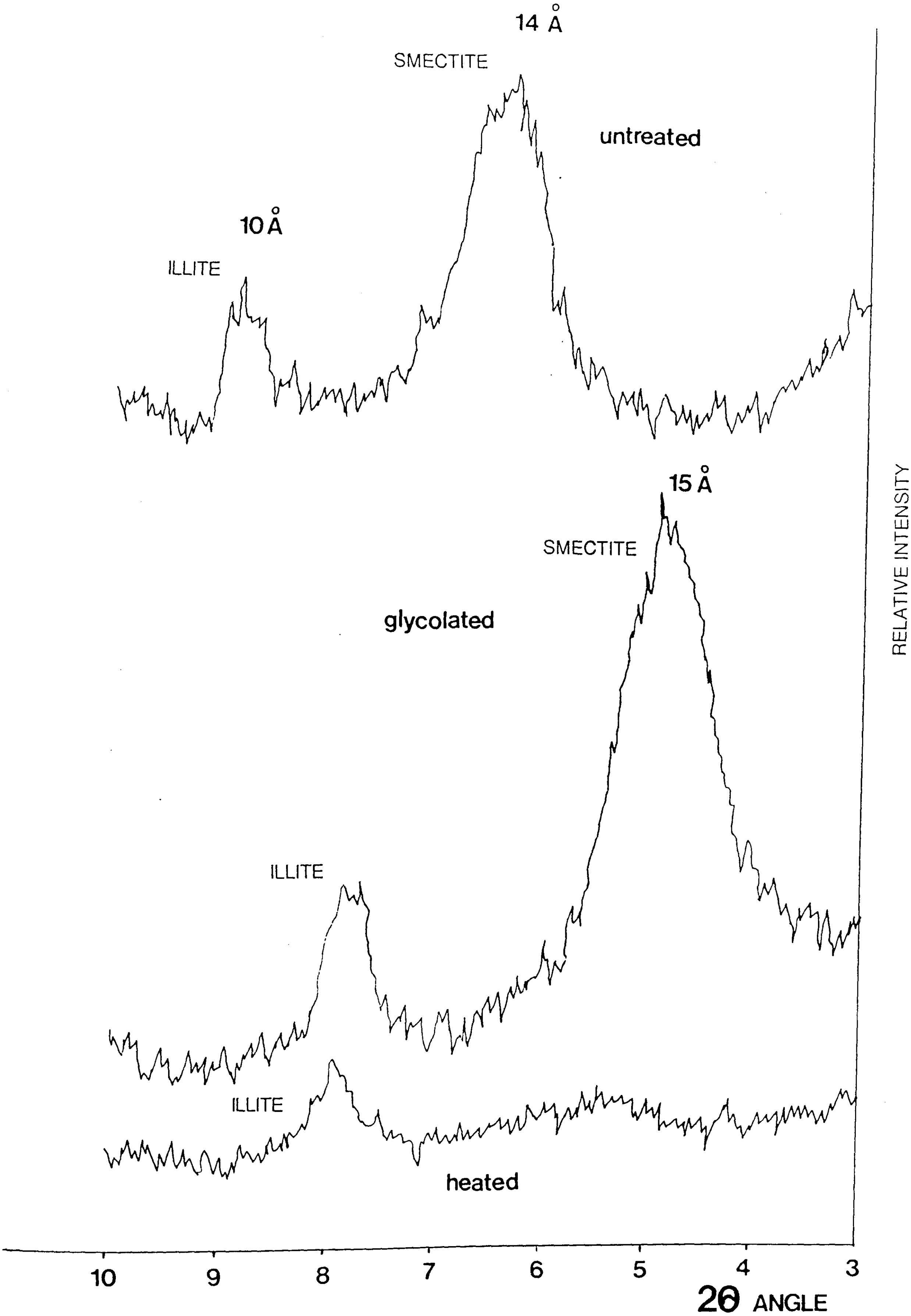


FIGURE 3.1 X-RAY DIFFRACTOGRAMS OF MIXED-LAYER CLAY

probably developed as a result of *in-situ* alteration of unstable iron-bearing silicates. The iron oxides and mixed-layer clays are then introduced into the sediments as amorphous iron hydroxide and iron bearing clays (Walker, 1976,1978). Alternatively, smectitic clays may be formed from the weathering of iron silicates, thus contributing to the authigenic clay component.

The latter morphology of pore-filling mixed layer- clays, which forms as aggregate patches within pore space, is thought to be of an allogenic nature. These clay aggregates were poorly crystalline when viewed in thin section at high power, and probably represent detrital, mechanically infiltrated clays.

Such differentiation between allogenic and authigenic clays can only be made qualitatively , as they are difficult to distinguish on the basis of morphology and structure. XRD analysis is unable to distinguish between pore- filling or pore- lining clays, and therefore any identification is based on the broad criteria of Wilson and Pittman, (1977).

XRD analyses indicate that the distribution of mixed-layer clays correlates with the distribution of haematite and the other iron oxides (Table 3.1). Like haematite, the mixed-layer clays are preferentially concentrated in certain facies within the sand body . Muds and silts rich in iron hydroxides and detrital iron-bearing clays would be preferentially concentrated in the finer grained sandstone and siltstone- bearing regions of the bar. Such regions, i.e. the Bar-Tail and Crevasse Splay / Overbank regions, would also have been exposed above the water-table at certain times, allowing oxidation of the silicates to occur. As indicated above the distribution of mixed-layer clays correlate well with the distribution of authigenic haematite, which suggests that the development of both mixed-layer clays and iron oxides is strongly facies-controlled. These phases occur preferentially in the facies where conditions are most suitable for their development. This explains the lack of mixed-layer clay development in the coarser grained sanstones of the Bar-Head facies.

This distribution also correlates with the distribution of allogenic mixed-layer clays. Such clays would represent the detrital 'fines' incorporated from the suspended bed load of the river system, and mechanically infiltrated into the sediments. As such, these to would be preferentially deposited in the downstream portion of the sand body (Bar-Tail), and in the flood-plain areas.

3.3 KAOLINITE

Within the examined bar samples, kaolinite occurs as an early authigenic phase, rather than as detrital grains. S.E.M. and X.R.D. analyses were used to recognise and distinguish kaolinite from other kandite group minerals. X.R.D. analysis was especially useful in distinguishing kaolinite and dickite, as these clays have similar authigenic morphologies under theS.E.M. (plate 3.7). Initial recognition of the clay phases in thin section was made using a standard petrological microscope. X.R.D. analyses were carried out on the <2mm. fraction using standard techniques (Pagan, 1980). The recognition of authigenic as opposed to detrital kaolinite was based on the criteria of Wilson & Pittman, (1977).

Authigenic kaolinite, occurs within these rocks as pseudohexagonal plates, most commonly as pore infill, but also occasionly as a pore-lining phase. The latter is more abundant in the Mid-Bar facies, although there is evidence of dissolution and replacement of the early grain-coating cement by the later carbonate cement.

The most common habit of the authigenic kaolinite is face-to-face (c-axis) stacking of pseudohexagonal plates. Individual plates range from 5-6µm. in diameter and are arranged as 'booklets' of platelets (plates 3.8, 3.9). Well-formed euhedral crystals are uncommon and most plates have a notched and grooved appearance (plate3.8). This could be an artifact of later dissolution, but may also be due to twinning in the crystals which can produce simlilar indentations (Mansfield & Bailey, 1972).

A veriform or vermicular morphology of authigenic kaolinite was also recognised by S.E.M. This latter kaolinite morphology was extremely rare and was visually estimated to occupy only an extremely small proportion of the original pore space. This unusual type of habit is thought to have resulted from extremely localised pH and Eh conditions of pore-fluid composition and local detrital grain population composition. It is not representative of the authigenesis as a whole.

Minor quartz overgrowths, or more correctly quartz 'outgrowths', were found intimately associated with authigenic kaolinite. Kaolinite and quartz are commonly found as intergrowths within the samples (plates 3.10, 3.11). This minor phase of authigenic quartz is thought to be an accessory

PLATE 3.7 S.E.M PHOTOGRAPH OF AUTHIGENIC KAOLINITE (K) INFILLING PORE SPACE (P 12.)

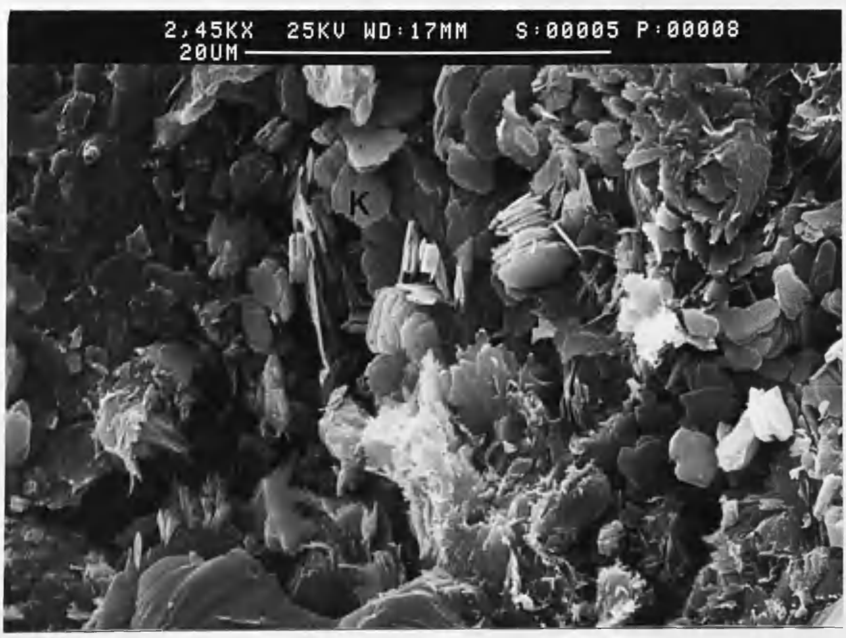


PLATE 3.8 S.E.M. PHOTOGRAPH OF AUTHIGENIC KAOLINITE 'PLATELETS' OR 'BOOKLETS' EXHIBITNG NOTCHED AND GROOVED GRAIN TERMINATIONS (P 13.)

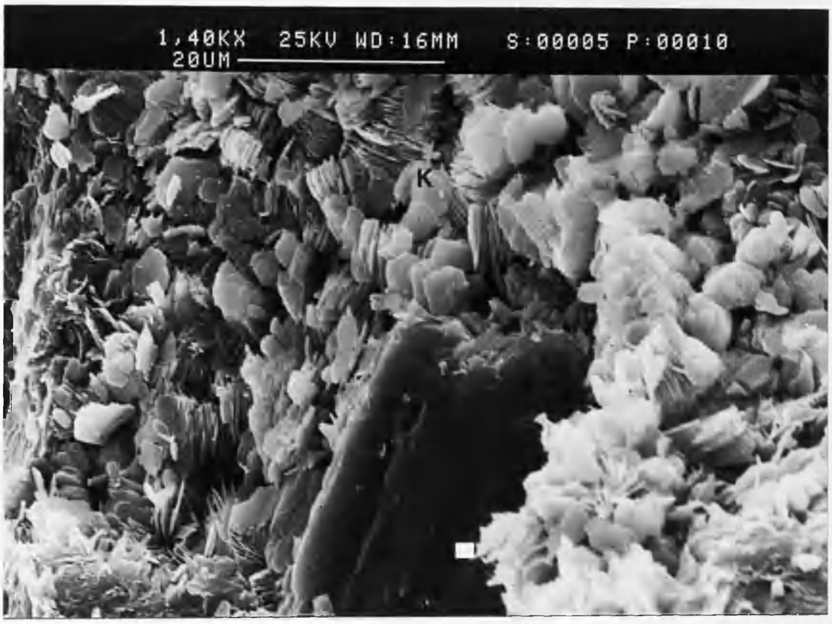


PLATE 3.9 S.E.M. PHOTOGRAPH OF KAOLINITE 'PLATELETS' AND 'BOOKLETS' (P 10.)

PLATE 3.10 S.E.M. PHOTOGRAPH OF AUTHIGENIC KAOLINITE AND QUARTZ 'INTERGROWTHS' (P 10.)

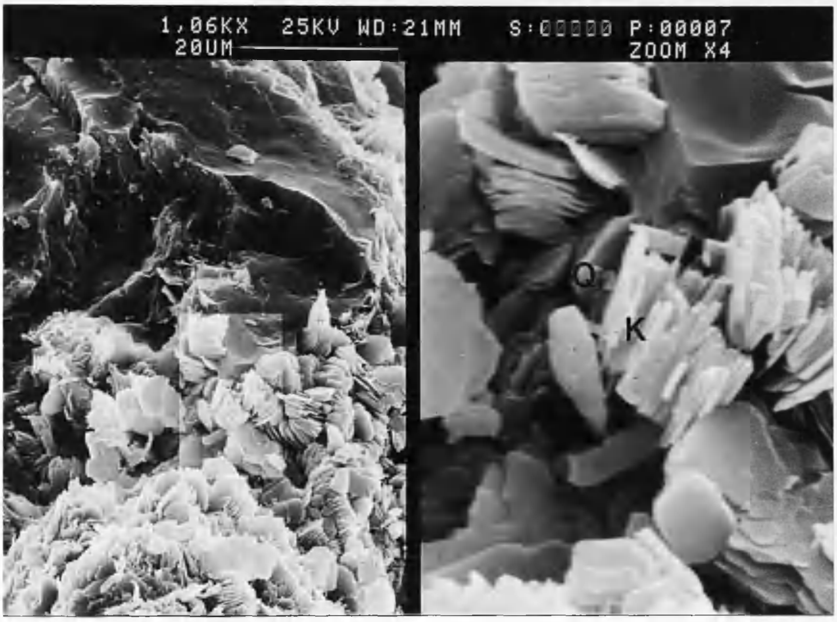


PLATE 3.11 S.E.M. PHOTOGRAPH OF AUTHIGENIC KAOLINITE AND QUARTZ 'INTERGROWTHS' (SPLIT SCREEN) (P 10.)

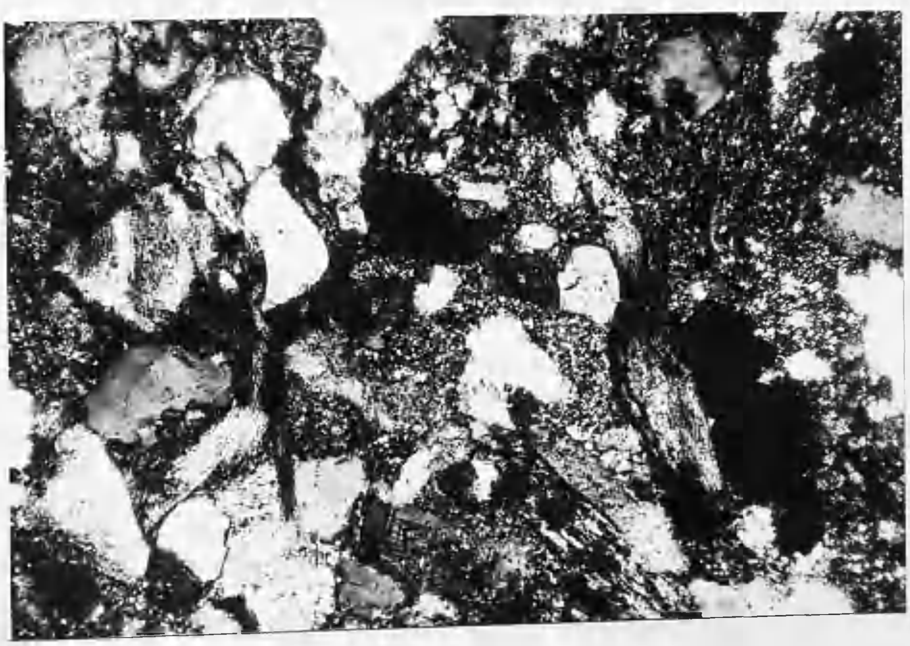


PLATE 3.12 PHOTOMICROGRAPH SHOWING 'SPONGE' LIKE TEXTURE IN FELDSPAR (F) GRAIN DUE TO PARTIAL LEACHING OF THE GRAIN (P 1.) (X 4O)

phase to the precipitation of the kaolinite (McBride, 1986).

Authigenic kaolinite in these sediments occurs predominately in the siltier grade facies, such as those encountered in the Bar-Tail facies (Table 3.1), and is found in only minor amounts cementing other bar facies. Outwith these bar facies, kaolinite occurs as a mixture of detrital and authigenic elements, the detrital component being the most abundant.

Kaolinite authigenesis is one of the first diagenetic changes to occur in fluvally-derived sequences. Because of the permeability and porosity variations within the sand body, kaolinite formation is largely controlled by detrital grain compositon and localised porewater and permeability conditions. These factors are themselves controlled by the depositional facies.Within the examined samples, detrital grains, particularly rock clasts showed varying degrees of dissolution and replacement by kaolinite. Volcanically derived grains, in particular exhibited a 'sponge'-like texture due to partial leaching of the grains (plate 3.12).Feldspar and other silicate mineral decomposition is associated with acidic dissolution, producing authigenic kaolinite by the following reaction.

$$2K\,Al\,Si_3O_8 + 2H^+ + H_2O = Al_2\,Si_2\,O_5\,(OH)_4 + 4\,Si\,O_2 + 2\,K^+$$

Orthoclase (or other detrital silicates) Kaolinite Quartz

(Helgeson,*et.al.*,1978)

Although the depositional pore- waters were originally meteorically- derived and would probably have had a pH of 7 - 7.5 (White, *et. al.*, 1963), the aerobic bacterial oxidation of organic material, such as plant tissue, produces carbonic acid. This may lead to the release of bicarbonate ions into solution generating the acidic porewaters required in the above reaction. These freshwater, low pH, positive Eh, and low salinity pore fluids could have resulted in the dissolution of silicates, leading to the formation of authigenic kaolinite (Bucke & Mankin, 1971; Curtis & Spears, 1971). This probably represents equilibration of the sediments with the depositional porewaters. This flushing by freshwater is widely believed to be responsible for the kaolinitization of many North Sea reservoir sequences (Blanche & Whitaker, 1978; Almon & Davies, 1979; Bjørlykke *et. al*., 1979) and a similar process may be applicable here.

Precipiitation of kaolinite is also known within shale-sandstone sequences, probably as a result of diagenetic reactions occurring within the shales. Inputs of exotic pore-waters result in fluxes, other than those of meteorically derived waters, leading to variation (on a localised scale) of authigenic kaolinite morphology (Land & Dutton, 1978; Boles, 1978; Boles & Franks, 1978; Foscolos & Powell, 1979).

The distribution of the authigenic kaolinite within the Crossgates sand body is facies-related. In the Bar-Tail facies where the authigenic kaolinite preferentially occurs, the original porosity and permeability of these regions e.g. Bar-Tail was poor. This was due to the presence of transported detrital and mixed-layer clays which were derived as accessories to the formation of haematite. These detrital and mixed-layer clays may have acted as nucleation points for the authigenic kaolinite to seed on to. This led to the preferential distribution of authigenic kaolinite within this facies.

In more porous facies, detrital and mixed-layer clays were not present in significant amounts, as these facies e.g Bar-Head were much coarser in nature due to the higher energy environment. Therefore nucleation sites were not readily present and authigenic kaolinite is therefore only poorly developed in this facies. Higher poroperm allowed the later flushing of pore fluids and may have resulted in the dissolution and removal of this early authigenic kaolinite. As a result, authigenic kaolinite is only sparsely developed in the coarser facies. It appears therefore, that distribution of early kaolinitic cements is both a function of original grain composition, energy of deposition, sediment supply, and ease of pore fluid movement.

The degradation of feldspars is not neccessarily a pre-requisite for the formation of kaolinite. Under tropical conditions, depositional pore waters may become saturated with alumina and silica from the breakdown of minerals to form lateritic soils, in sufficient amounts for the primary precipitation of kaolinite to take place (White et. al., 1963; Tardy, 1971). Veriform kaolinite is known to occur in modern-day tropical soils (Fitzpatrick, 1980). This may have led to the formation of the veriform kaolinite seen within the Crossgates samples resulting from the influence of extremely localised pH- Eh conditons.

SUMMARY.

The development of authigenic kaolinite within this sequence, probably results from the *in-situ* degradation of detrital silicate material. These silicates, in the presence of acidic fluids, undergo dissolution leading to the formation of authigenic kaolinite and quartz. These occur as intergrowths within the Crossgates sequence. The distribution of the kaolinite is controlled by the depositional facies as this is the primary control on the detrital grain components and hence the development of authigenic kaolinite.The depositional conditions influence the composition of the facies and therefore the composition of the rocks that that facies contains.

3.4 QUARTZ

Small incipient euhedral quartz overgrowths intergrown with authigenic clays occur in a few samples. They occur as 'outgrowths' on earlier detrital quartz grains, usually in the form of microgrowths on the edge or corner of a detrital grain (plates 3.10, 3.11, 3.13). A possible intra-formational source for the silica is the degradation of feldspars into kaolinite as outlined above, with the production of SiO_2 as a biproduct of the reaction. Evidence for this is given by the presence of kaolinite platelets embedded in the quartz overgrowths (plates 3.8, 3.9). It therefore is likely that both authigenic phases precipitated at the same time and that the minor amounts of authigenic quartz were fomed during the precipitation of kaolinite (McBride, 1986).

3.5 CARBONATE

Two phases of authigenic carbonate, can be recognised in the sedimentary sequence at Crossgates.

1. Precipitation of 'early ' calcite from pore fluids.
2. Calcitic veining developed as a result of the re-mobilisation of earlier authigenic calcite during the Stephanian igneous activity.

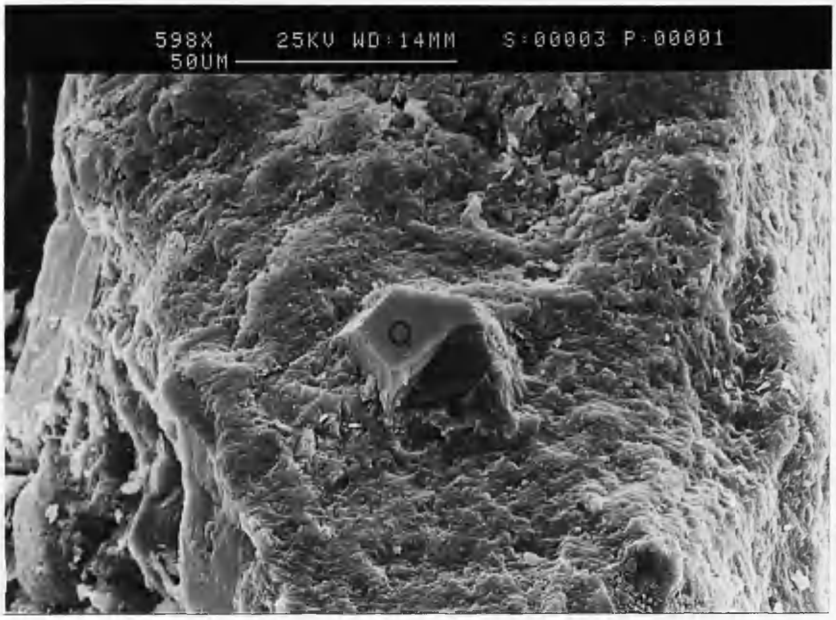


PLATE 3.13 S.E.M. PHOTOGRAPH OF AUTHIGENIC QUARTZ 'OUTGROWTH' (Q) ON DETRITAL QUARTZ GRAIN (P 11.)

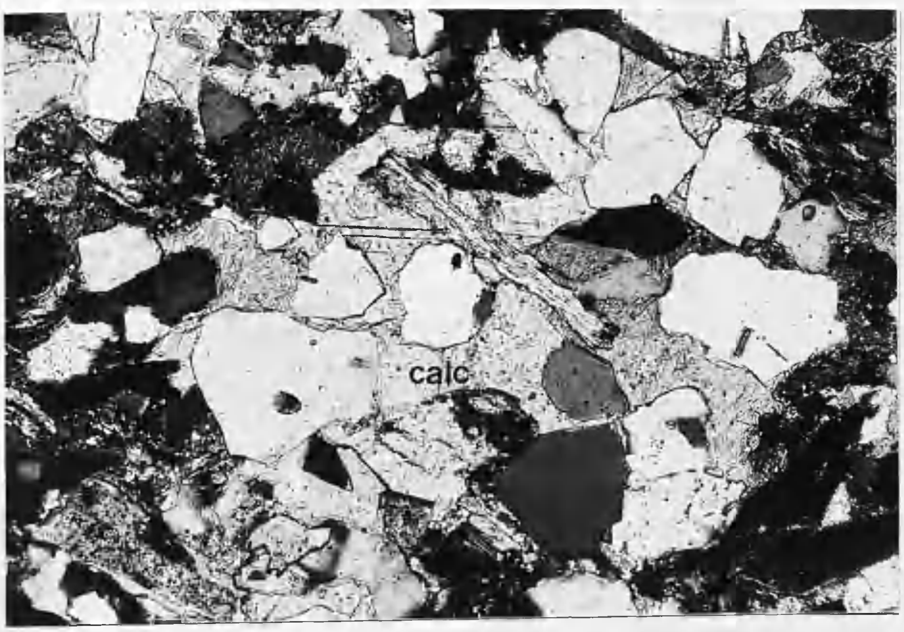


PLATE 3.14 PHOTOMICROGRAPH OF PORE FILLING CALCITE (CALC) CEMENT, ILLUSTRATING RETENTION OF ORIGINAL PORE GEOMETRY (P 20.) (X 40)

1. 'EARLY' CALCITE

'Early ' calcite occurs pervasively in all of the bar facies. In thin section, it typically occurs as a pore-filling calcite cement (plate 3.14). In some samples a poikilotopic calcite cement is well developed which may wholly enclose detrital quartz and feldspar grains (plate 3.15). Such areas of poikilotopic cement occur in the Bar-Head facies of the bar. This variation in the type of cementation is thought to result from variation in the original available pore- size, and subsequently the porosity / permeability.

In facies where the porosity was poor, at the time of carbonate precipitation, then the calcitic cement occurs only sporadically in the the rock, infilling the remaining porosity [plate3.16). This porosity may only be present as micropores and spaces throughout the facies due to cementation by earlier authigenic phases. Typically, this occurs in the Bar-Tail, where original porosity was poor and subsequently greatly reduced by the development of haematite and mixed layer clays. These grain coatings can restrict the diameter of the pore throats and so provide effective barriers to the passage of pore fluids, therefore restricting the degree of pore-water precipitation which occurred in the affected facies. This is well exhibited in the sediments of the Bar-Tail facies, where the carbonate is only poorly developed as a result of the above control by earlier authigenic components.

Where the available porosity and permeability were much higher at the time of carbonate precipitation (typically in the Bar- Head facies), then zones of poikilotopic calcite cement are developed (refer to plate 3.15). This is a result of the greater porosities and permeabilities in these facies, where precipitating pore fluids have been able to circulate through the sands with little restriction . This is reflected in the well- developed calcite cement of the Bar-Head facies (plate 3.17). Within this facies, a 'floating' texture is commonly seen, with large areas of poikilotopic cement occupying original pore- space and detrital grains often 'floating ' in the cement (plate 3. 15) In many samples the original pore-space geometry has been preserved by the calcite cement infill (plate 3. 14), indicating that the precipitation of the carbonate occurred prior to significant compaction of the sediment and therefore 'early 'in the diagenetic history of the sediments.

The distribution of the 'early ' calcite cement reflects the available porosity and permeability within the sand bar and highlights the porosity / permeability contrasts within the sand -body. Under

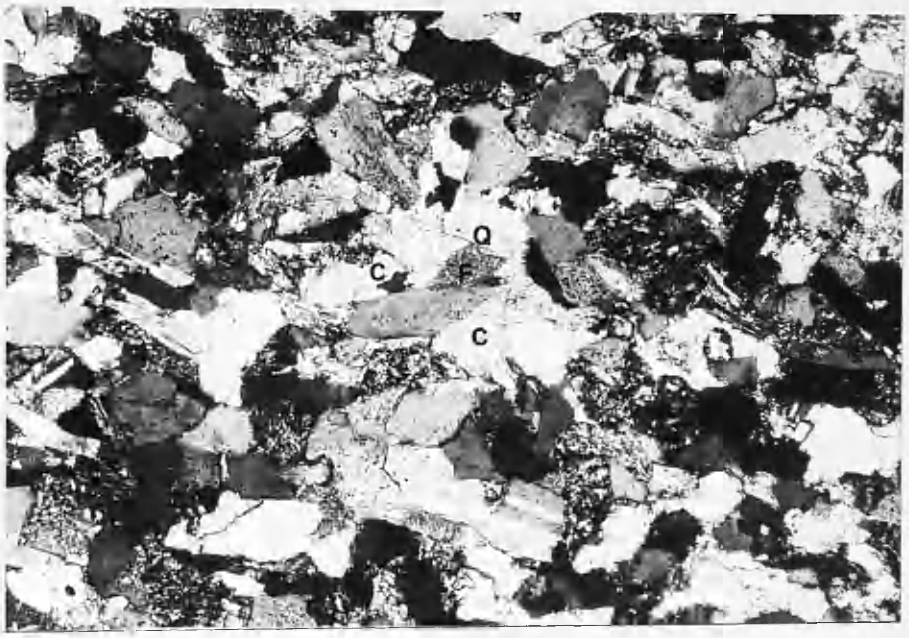


PLATE 3.15 PHOTOMICROGRAPH OF POIKILOTOPIC CEMENT ENCLOSING DETRITAL QUARTZ (Q) AND FELDSPAR (F) GRAINS (P 19.) (X 40)

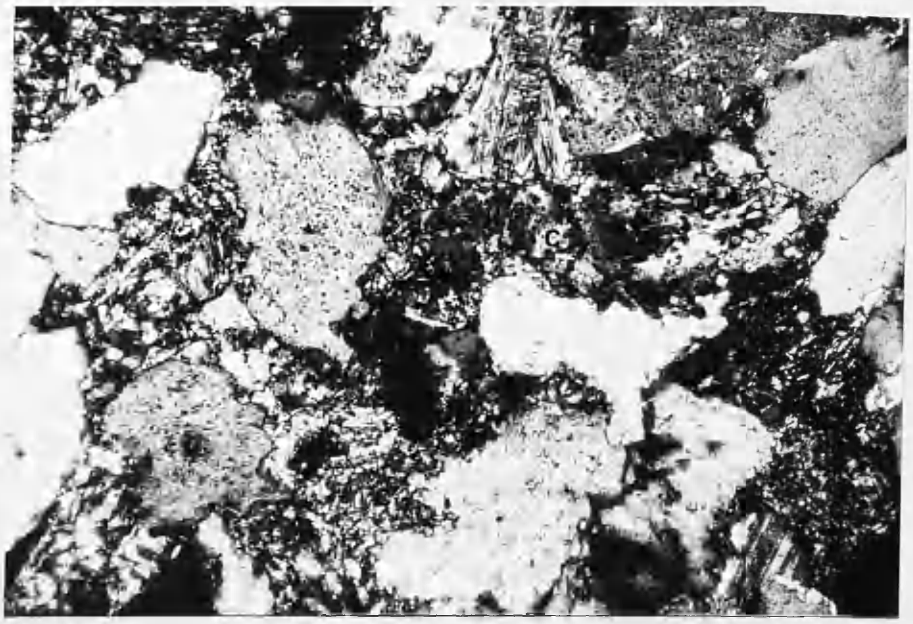


PLATE 3.16 PHOTOMICROGRAPH SHOWING MICROPORES INFILLED BY CALCITE (C) (P 8.) (X 40)

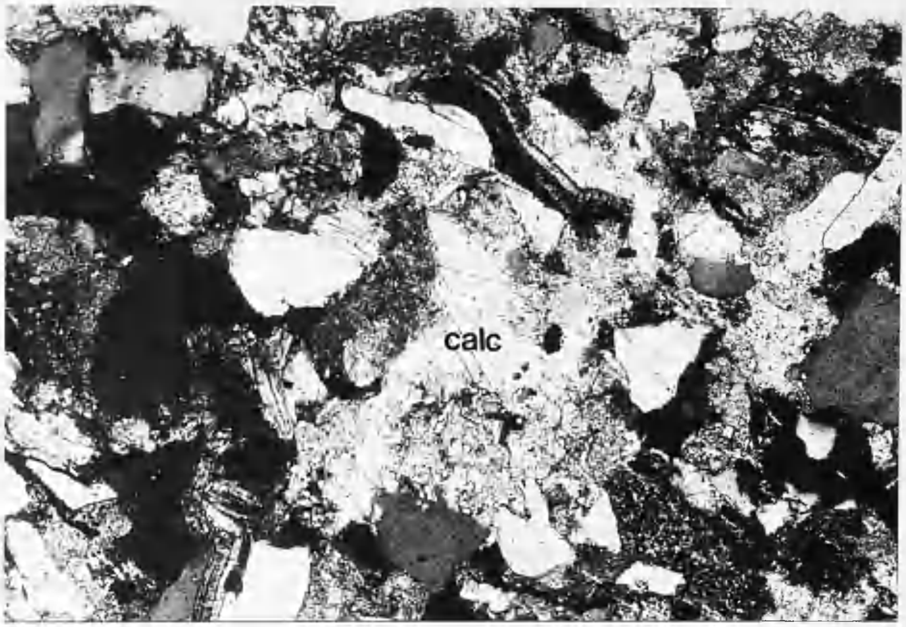


PLATE 3.17 PHOTOMICROGRAPH OF WELL DEVELOPED POIKILOTOPIC CALCITE CEMENT WITHIN THE BAR-HEAD FACIES (P 19.) (X 40)

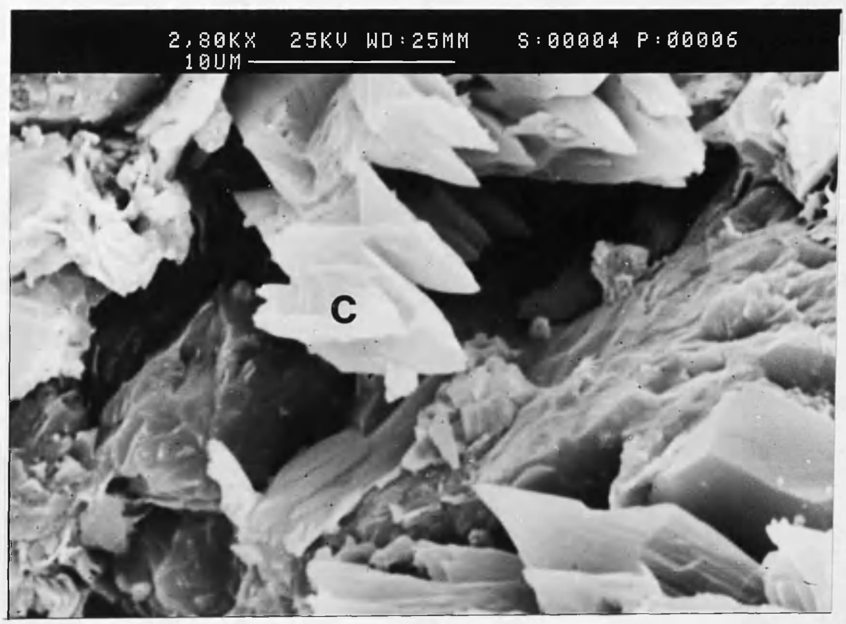


PLATE 3.18 S.E.M. PHOTOGRAPH OF RHOMBIC AUTHIGENIC CALCITE (C) INFILLING PORE SPACE (P 17.)

the S.E.M., this 'early 'calcite occurs as a blocky pore- filling cement, showing the rhombic morphology typical of calcite (plate 3. 18). EDAX analysis indicates that the spectra of the mineral consists primarily of calcium (figure 3. 2). Since both carbon and oxygen are too 'light' to be detected by the EDAX facility, they do not appear on the spectra. No significant amounts of iron were detected in the spectra, indicating a non-ferroan calcite.

As indicated above, calcite is pervasive in all of the bar facies, although its abundance within individual facies may vary. It is predominantly pore- filling and in part replaces earlier cements and detrital sillicates. Dissolution of detrital silicates is commonly observed in the form of embayments and aggressive dissolution of the detrital grain (plate 3. 19). Such grains exhibit an irregular outline formed as a result of dissolution, rather than as a primary textural feature. Within the calcite cement, 'ghosts' of quartz grains with only a faint outline of their former presence (plate 3. 20) can be seen. These grains have sufferred total dissolution and replacement by the precipitating cement. These completely dissolved grains and the considerable dissolution of other detrital grains indicate that the pore-fluid circulating at this time was extremely corrosive.

Some areas of cement, particularily those in facies where haematite and interstitial clay are present, show disruption of the prior cements. The early grain-coating haematite and clays appear to have been re-deposited within the the carbonate cement as the grain-coat is disrupted by the later pore fluid, commonly resulting in 'reddening' of the cement (plate 3. 21). The EDAX analysis of such areas yield spectra (figure 3.3) which consist primarily of calcium, but also contain minor amounts of silicon, aluminium and potassium. The latter elements are probably due to the clay inclusions within the calcite cement.

Authigenic anatase is commonly intergrown with the carbonate, and therefore was most likely co-precipitated with the calcite from the same pore fluid.

1.1 CATHODOLUMINESCENCE

The technique of cathodoluminescence is an invaluable tool in clarifying the diagenetic history of a sediment sequence, with especial reference to the understanding of zonation of cements not normally reconisable using normal petrographic techniques. In this study

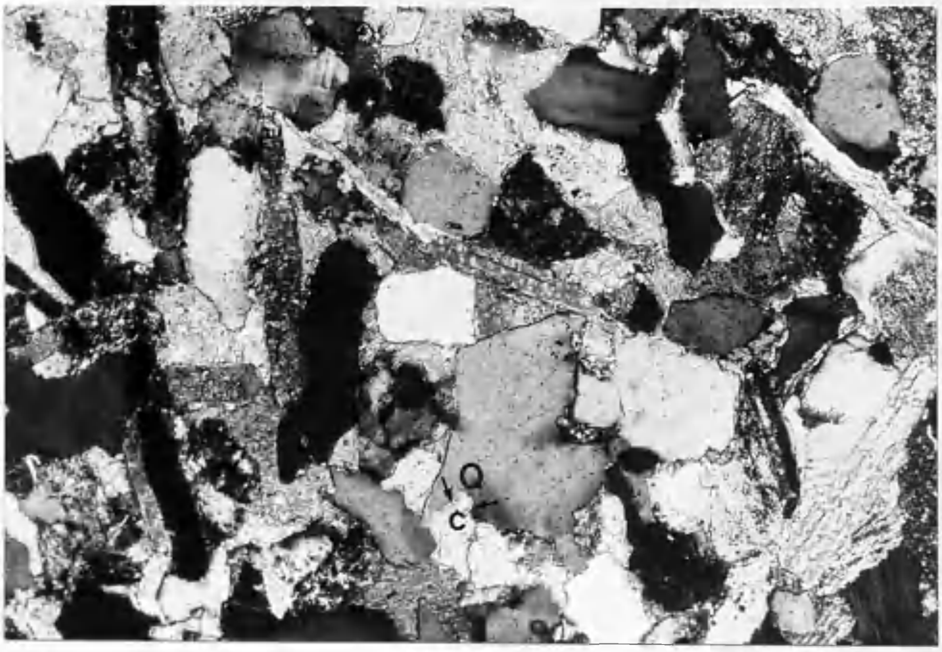


PLATE 3.19 PHOTOMICROGRAPH OF AGGRESIVE DISSOLUTION OF DETRITAL SILICATES (Q) FORMING GRAIN EMBAYMENTS (P 17.) (X 40)

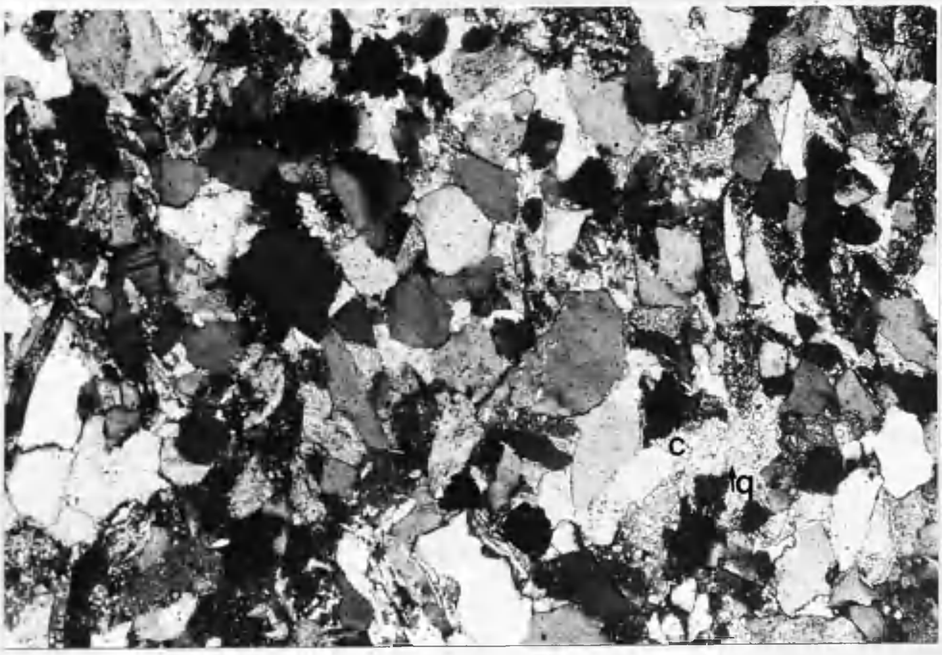


PLATE 3.20 PHOTOMICROGRAPH ILLUSTRATING 'GHOSTING' OF DETRITAL QUARTZ GRAIN DUE TO TOTAL REPLACEMENT BY CALCITE CEMENT (P 19.) (X 40)

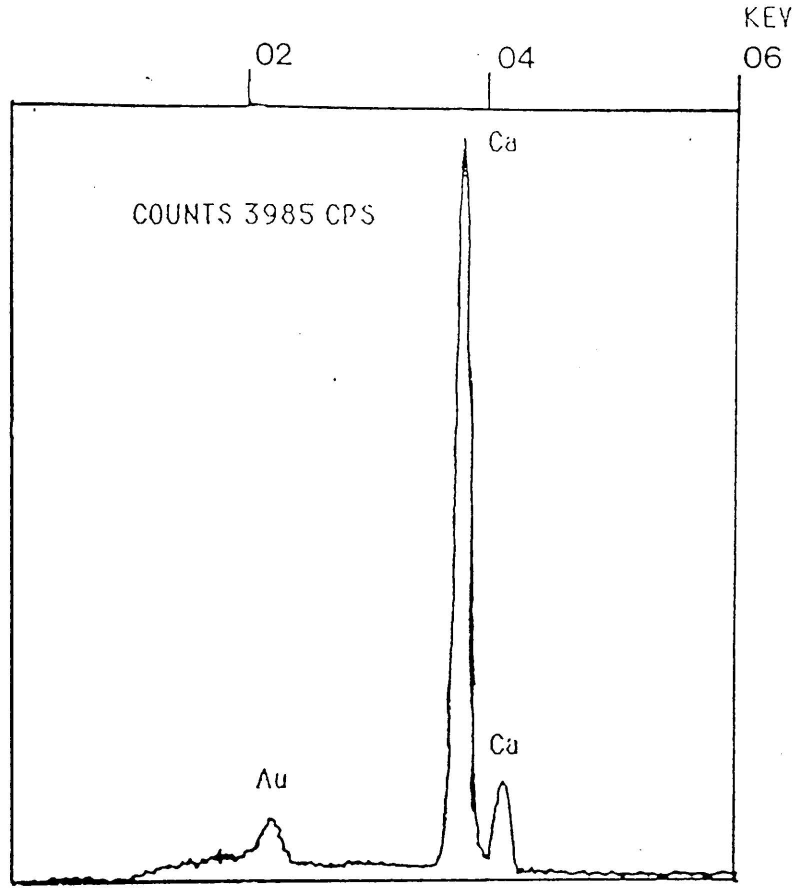


FIGURE 3.2 EDAX SPECTRA OF NON-FERROAN CALCITE

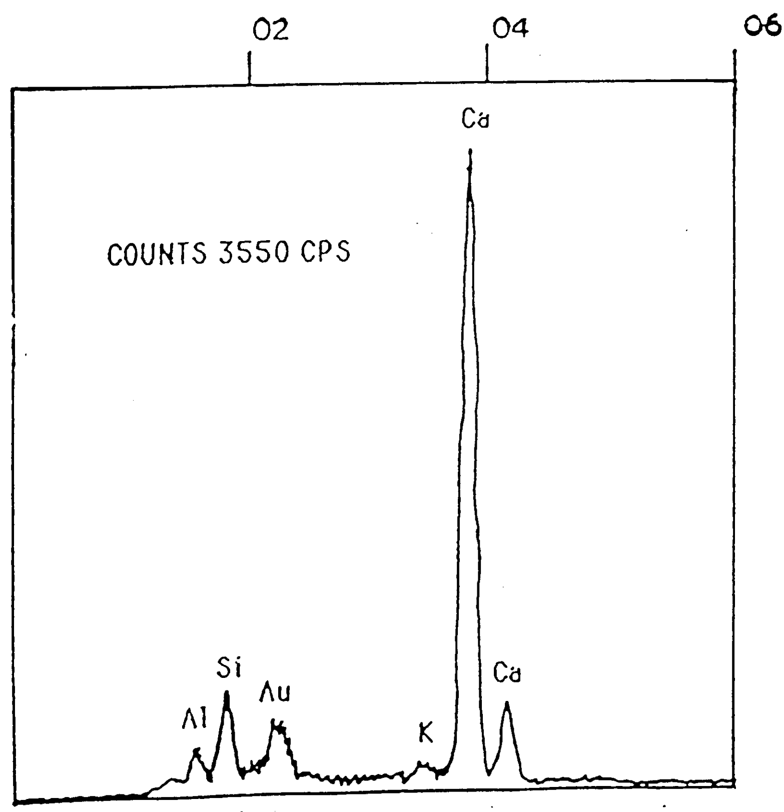


FIGURE 3.3 EDAX SPECTRA OF CALCITE CEMENT WITH SI, AL, AND K PEAKS DUE TO CLAY INCLUSIONS WITHIN THE CEMENT

PLATE 3.21 PHOTOMICROGRAPH ILLUSTRATING DISCOLOURATION OF CARBONATE CEMENT DUE TO DISRUPTION OF EARLIER HAEMATIE GRAIN COAT AND SUBSEQUENT RE-DISTRIBUTION IN THE LATER CARBONATE CEMENT (P 2.) (X 40)

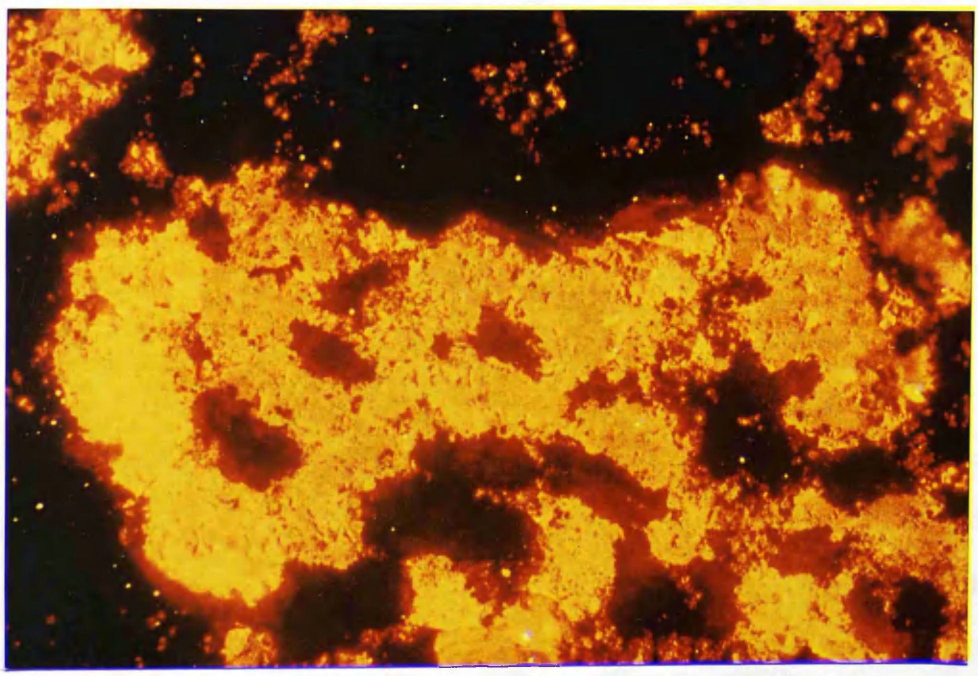


PLATE 3.22 CATHODOLUMINESCENCE PHOTOMICROGRAPH SHOWING DULL MOTTLED ORANGE AUTHIGENIC CALCITE CEMENT

the cathodoluminescence of the bar facies was studied using a Technosyn Cold Luminoscope, at Britoil P.l.c., Glasgow.

Cathodoluminescence work was undertaken on samples from each of the bar- facies. Inter-channel sediments were also examined. The results are presented below :

FACIES	CATHODOLUMINESCENCE
Bar Tail	Dull, mottled, orange irregular luminescing calcite
Mid Bar	Mottled, dull, orange irregular luminescing calcite
Bar Head	Dull, orange irregular luminescing calcite, mottled, no zonation
Crevasse Splay / Overbank	Dull, mottled, orange irregular luminescing calcite

The typical luminescence of the 'early ' carbonate authigenic cement is a dull, mottled orange luminescing calcite (plate 3. 22). Each of the different facies shows similar luminescence properties and although the luminescence is slightly irregular, no zonation of the carbonate cement was observed. The slight irregular variation in luminescence is thought to arise from minor variation in the Fe and /or Mn distribution within the calcite itself (Pierson, 1981).

The lack of compositional zoning (plates 3. 23 and 3. 24) within the 'early ' calcite indicates that precipitation of this cement occurred as a single, pervasive generation non ferroan calcite. (See also section 1.2) The aggressive corrosion of detrital grains is also well shown by cathodoluminescence observation (plate 3.24).

Cathodoluminescence and petrographic analysis indicate that this 'early ', non-ferroan calcite was the main phase of carbonate cement precipitation within these sediments and that it occurred in a single pervasive precipitation event which occurred prior to significant compaction of the sediments.The most likely origin for this carbonate cement is as a precipitate from Lower Devonian meteoric waters.

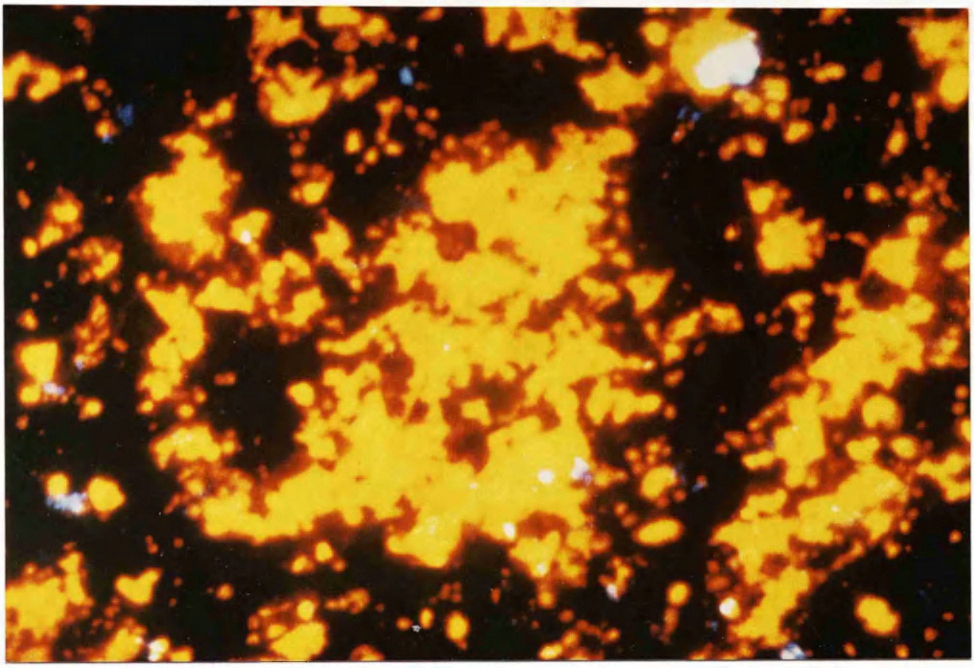


PLATE 3.23 CATHODOLUMINESCENCE PHOTOMICROGRAPH SHOWINGSINGLE GENERATION NON-FERROAN CALCITE WITH NO COMPOSITIONAL ZONATION

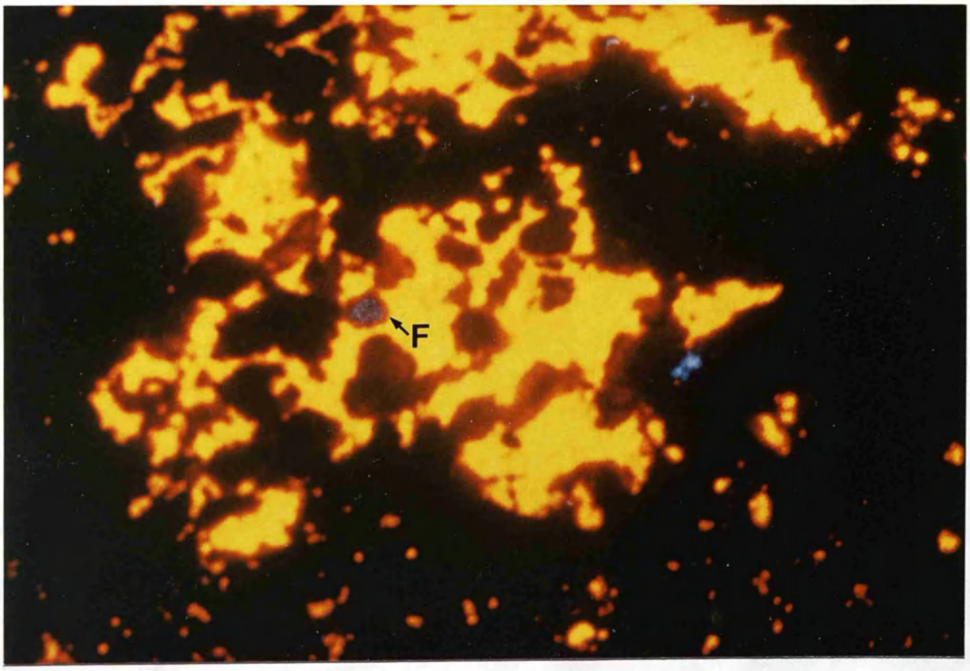


PLATE 3.24 CATHODOLUMINESCENCE PHOTOMICROGRAPH SHOWING A SINGLE GENERATION CALCITE WITH ACCOMPANYING AGGRESIVE DISSOLUTION OF A FELDSPAR GRAIN

1.2 MICROPROBE ANALYSIS

Electron microprobe analyses were performed at the University of St. Andrews using a Jeol S.E.M. equipped with an electron microprobe. The 'spot size ' of the electron beam was 1 μm.

The microprobe data show little elemental variation throughout the bar-facies (Table 3.2). No facies differentiation could be detected within the cement samples. The fine- grained nature of the rocks and the presence of clay particles within the cement made it difficult to obtain uncontaminated analyses from the Crevasse Splay / Overbank facies, which accounts for the very minor variation observed in samples from this facies. Analyses of calcite cement in samples from the vicinity of the dyke show differences because of metamorphic hydrothermal re-distribution.

Microprobe analysis suggest that the calcite cement was precipitated as a single generation and is non-ferroan in nature. No zonation could be detected in transects across cement patches or between facies. This contrasts with the analyses of Saigal (1985), and Saigal and Walton (1988), who noted zonation in calcretised sediments of the Garvock Group. The evidence from the Crossgates sediments may reflect a different mode of formation for these cements rather than the result of primary pedological events as postulated by Saigal, (1985) and Saigal and Walton (1988).

2. CALCITE VEINING

The second phase of authigenic carbonate precipitation is the development of calcite veining in the sediments adjacent to the dyke intrusion. These veins occur as 2-5 mm. wide thread-like structures (plate 3. 25), which originate in the sediment body and are 'injected' into the dyke. In thin section, the veins are composed of polycrystalline calcite which are complexly intergrown. These veins post-date the earlier phase of authigenic calcite, since they frequently cross-cut areas of earlier calcite cement. The margins of the dyke show a slight degree of carbonation and within this zone of approximately 1-2m. thickness, feldspar phenocrysts have been pseudomorphed by calcite. The intrusion of this dyke may have caused localised hydrothermal alteration of the adjacent sediment sequence, resulting in the re-mobilisation of part of the earlier pervasive carbonate as calcite veins. This conclusion is supported by both the petrographic and stable isotope data .

MICROPROBE DATA FOR THE CROSSGATES BAR SEDIMENTARY FACIES

			MOLE %			
SAMPLE	DESCRIPTION	n	CaCO	MgCO	FeCO	MnCO
BAR-HEAD						
P 18	Poik. cement	3	97.9%	0.9%	0.6%	0.6%
P 20	Poik. cement	7	99.1%	0.6%	0.0%	0.3%
MID-BAR						
P10	Poik. cement	11	97.8%	0.9%	0.6%	0.7%
BAR-TAIL						
P 7	Poik. cement	5	98.2%	0.6%	0.5%	0.7%
P 8	Poik. cement	6	98.3%	0.7%	0.3%	0.7%
CREVASSE SPLAY / OVERBANK						
P 23*	Poik. cement	15	95.8%	1.6%	0.7%	1.9%
P 26*	Poik. cement	6	96.0%	2.2%	1.2%	0.6%
BAR-TAIL, LATE VEIN						
P 1a	Vein	5	98.0%	0.5%	0.4%	1.1%
BAR-TAIL, DYKE AFFECTED						
P 1**	Cement	3	96.6%	1.9%	0.8%	0.7%
P 2**	Cement	4	97.4%	1.4%	0.6%	0.6%

* Samples P 23,26 show 'contamination' by detrital infiltrated clays, i.e. are not 'clean' carbonate

** Samples P1,2 are affected by the intrusion of a late Carboniferous dyke.

n Refers to the number of analysis performed per sample.

TABLE 3.2 MICROPROBE DATA FOR THE CROSSGATES BAR SEDIMENTARY FACIES

PLATE 3.25 PHOTOMICROGRAPH OF THREAD-LIKE POLYCRYSTALLINE CALCITE VEIN, THESE ARE DEVELOPED IN SEDIMENTS WHICH HAVE BEEN SUBJECT TO A THERMAL OVERPRINT BY THE DYKE (P1.) (X80)

PLATE 3.26 S.E.M. PHOTOGRAPH OF TETRAGONAL AUTHIGENIC ANATASE CRYSTALS (P 18.)

SUMMARY

The precipitation of authigenic carbonate occurs as two phases; an early pore-filling pervasive, non-ferroan single generation calcite cement and a second later phase of carbonate veining resulting from igneous activity during the Carboniferous.

The first phase of calcite was probably precipitated from Lower Devonian meteoric waters (See chapter four), the carbonate most probably being derived from the pedogenic sequences of the Garvock Group. The second phase of carbonate precipitation resulted from the localised hydrothermal alteration of sediments adjacent to the intrusion, leading to re-mobilisation of part of the earlier authigenic calcite in the affected region and its subsequent re-precipitation in the form of calcite veins.

3.6 ANATASE

Contemporaneous with the pore- filling 'early' calcite, a pervasive phase of authigenic anatase is developed. This diagenetic phase occurs as intergrowths with the calcite cement, and is thought to be a co-precipitate with the calcite from pore fluids.

TiO_2 polymorphs can only be distinguished from each other by optical and X.R.D. techniques. EDAX analysis was used to identify the mineral phase as TiO_2 (figure 3.4) and S.E.M. observation was used to distinguish anatase from the other TiO_2 polymorphs of rutile and brookite. Under S.E.M., anatase occurs as tetragonal crystals which are usually intergrown with blocky calcite (plates 3. 26 and 3.27).

Since both calcite and anatase are co-precipitated in the sediments, it is likely that both precipitated from the same pore fluid, at the same time. This pore fluid must therefore have been substantially enriched in titanium ions at this time. It seems unlikely that the titanium could have been derived wholly from the *in-situ* breakdown of titaniferous-bearing minerals, since the fluid must have been substantially enriched with respect to this element in order to precipitate the amount of authigenic anatase present within these sediments. Therefore, the pore fluid must have obtained an additional supply of titanium ions. This enrichment may have come from leaching of the underlying

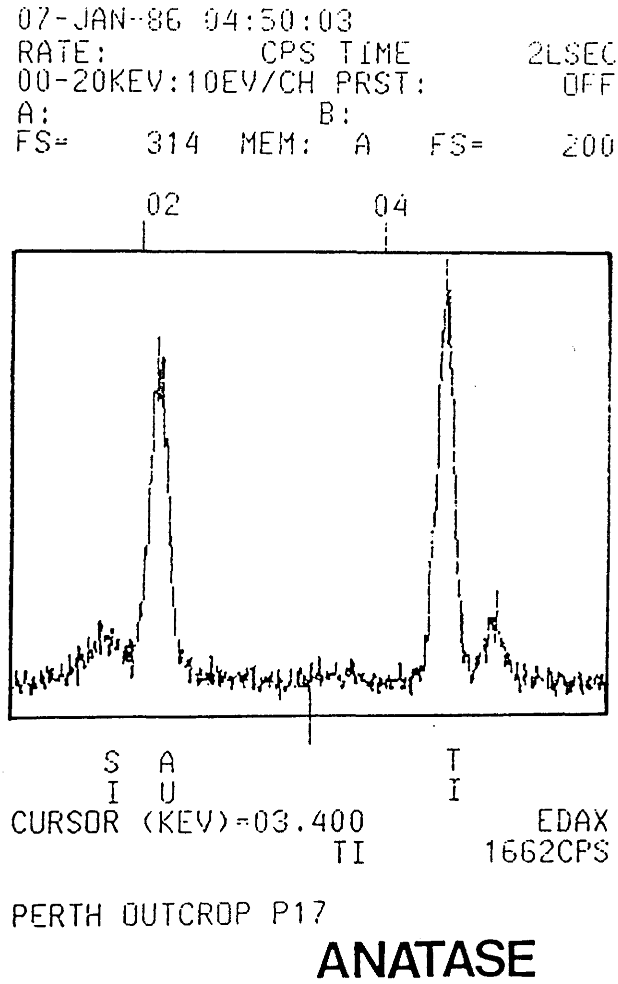


FIGURE 3.4 EDAX SPECTRA OF AUTHIGENIC ANATASE

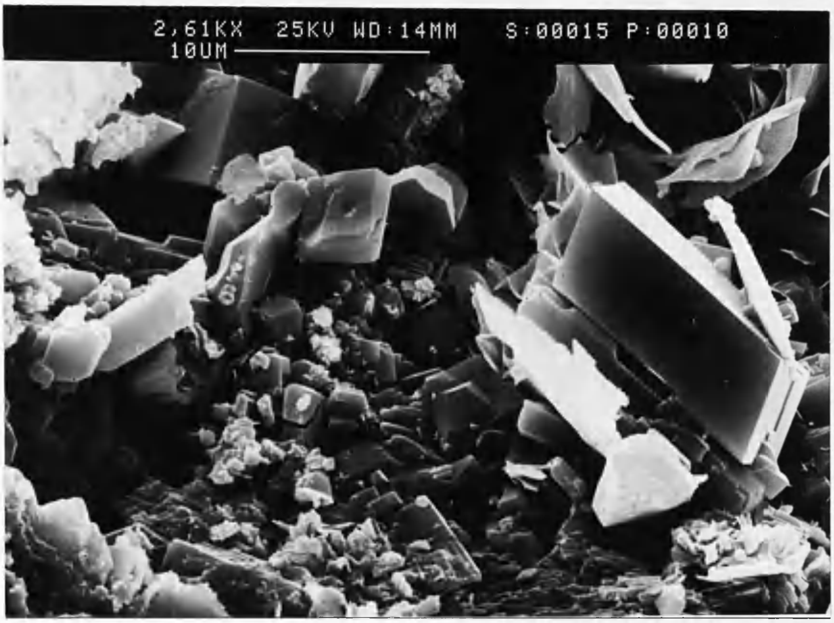


PLATE 3.27 S.E.M. PHOTOGRAPH OF TETRAGONAL ANATASE INTERGROWN WITH BLOCKY CALCITE (P 18.)

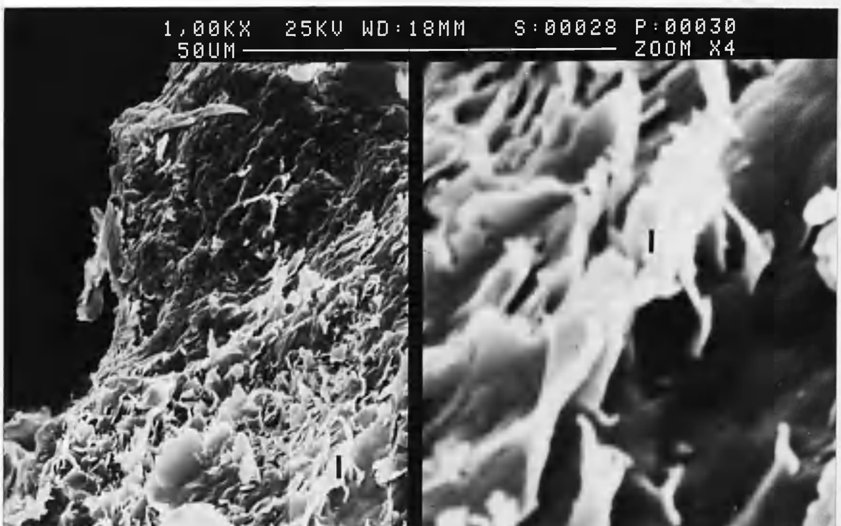


PLATE 3.28 S.E.M. PHOTOGRAPH OF FIBROUS PORE-BRIDGING ILLITE DEVELOPING ON EARLIER GRAIN COAT (P 1.)

volcanic sequence, titanium derived from this source being added to the pore fluid solution.

3. 7 ILLITE

Authigenic illite (identified by S.E.M. and XRD techniques), occurs within the Bar-Tail facies and exhibits a fibrous pore-bridging habit (plate 3. 28). These fibres commonly occur in the form of fine filaments which decrease in diameter from their point of origin towards the pore space. These filaments are observed to emanate from the edges of earlier grains of a detrital and diagenetic nature. Individual filaments may be several microns in length and range in thickness from 2 to 20 ηm (Guven et.al.,1980; Srodon and Eberl, 1984; McHardy *et al.*, 1982; Nadeau, 1985.).

Macchi (1987) has postulated a probable association between fibrous illite growth and the presence of a pre-existing grain- coating or pore-lining clay. These substrate clays may be of diagenetic origin or as mechanically-infiltrated clay, with the illite fibres developing from the edges of the anhedral clay plates. Such evidence suggests the formation of ordered illite as a result of the transformation of earlier mixed- layer illitic and smectitic clays during burial similar, to the situation seen in the Gulf Coast sequences of the U.S. (Boles and Franks 1979). The fibrous growths represent new crystal growth from nucleation sites as the smectite-illite transformation takes place.

The distribution of authigenic illite within the sand body closely resembles that of the earlier mixed-layer clays, suggesting that there may be a strong correlation between the fibrous illite growth and the presence of a pre-existing substrate clay. This distribution is stongly polarised in favour of the clay-rich facies of the bar, in particular the Bar-Tail Facies and the Crevasse-Splay / Overbank regions.

Minor formation of illite may have continued after the intrusion of the Stephanian dyke, but the main phase of illite generation occurred prior to intrusion of the dyke.

3.8 CHLORITE

Authigenic chlorite occurs as both late-stage grain coatings and honeycomb pore-lining crystals and plates (plate 3.29), (Hayes, 1970). This authigenic phase post-dates all other cement

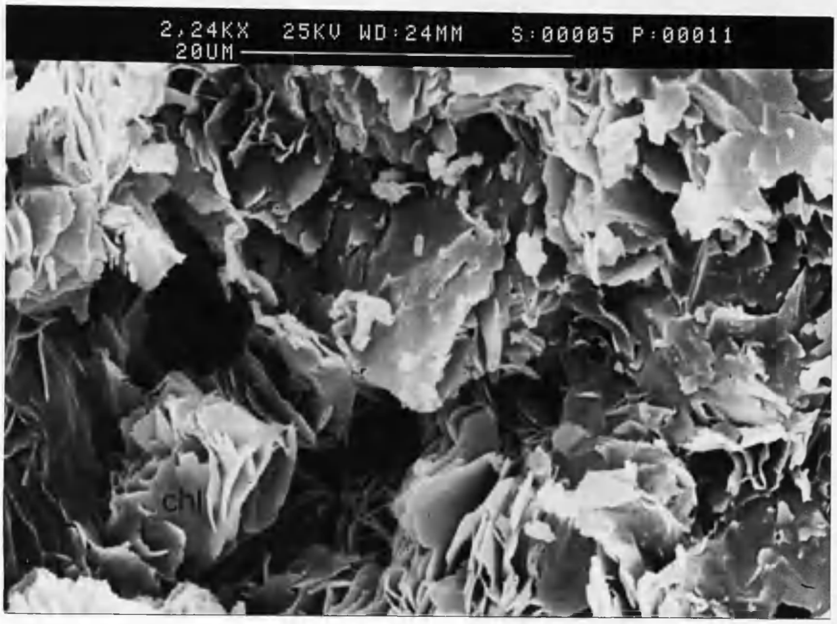


PLATE 3.29 S.E.M. PHOTOGRAPH ILLUSTRATING THE FORMATION OF CHLORITE (CHL) PLATES AND LATHS (P1.)

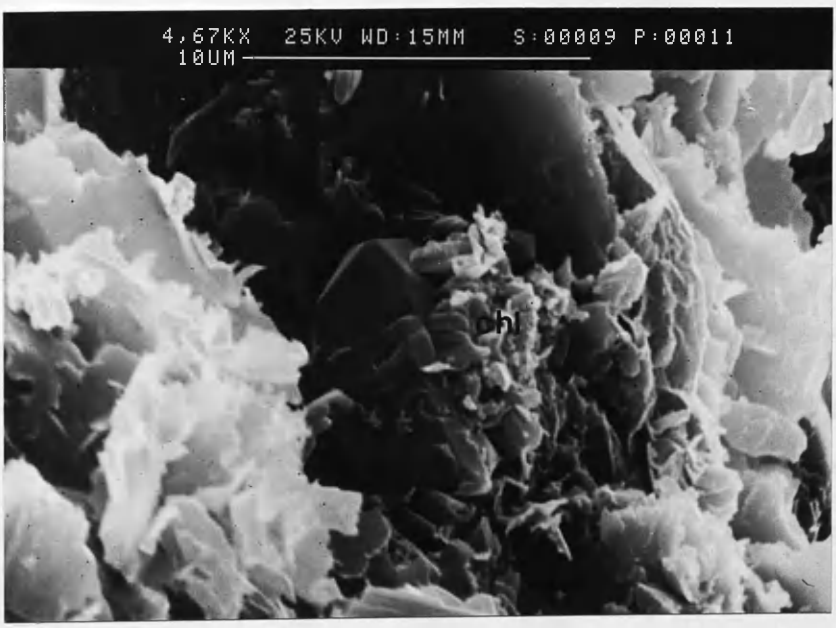


PLATE 3.30 S.E.M. PHOTOGRAPH SHOWING THE DEVELOPMENT OF CHLORITE (CHL) AS OUTGROWTHS FROM DETRITAL GRAIN EDGE (P 2.)

phases. In thin section, where the pore lining / grain coat is quite thick, a greenish chloritic rim could be detected on some sediment grains.

Under the S.E.M., chlorite occurs as well-crystallised platelets which form outgrowths from the edges of the host grains (plate 3.30). These crystals are often densely packed and, show random orientation. In the honeycomb pore-lining chlorite, the distinctive morphology arises from the orientation of the chlorite platelets. These curve and intersect to form a cell- like structure or honeycomb (plate 3.31) (Wilson and Pittman, 1977).

E.D.A.X. analysis indicates the chlorite to be an iron-rich variety, containing the major elements Si, Al, Mg, and Fe (figure 3.5) . XRD analysis further indicates the chlorite to be a partially swelling variety (figure 3.6). This 'swelling ' property may have an effect on permeability since it renders the chlorite water- sensitive and thus sensitive to pore-fluid composition, (Curtis *et al.*, 1984).

The timing and distribution of the authigenic chlorite is thought to reflect its probable origin. The occurrence of authigenic chlorite is localised to the sediments adjacent to the dyke intrusion and its abundance decreases away from the dyke. Therefore, this phase of authigenic chlorite is thought to result from localised hydrothermal alteration of ferromagnesian minerals, e.g chloritisation of biotite (plate 3.32), in sediments adjacent to the intrusion.

3.9 SUMMARY

The paragenetic sequence for the sequence can be summarised in figures 3.7 and 3.8, and as follows : Grain- coating haematite and mixed layer clays are developed. These phases show evidence of both pre and syn-depositional origin, although most of their development in these sediments is of diagenetic origin. Subsequent pore-filling kaolinite and associated minor quartz overgrowths are prominent in the silty-grade facies. Calcite and contemporaneous anatase are pervasive, and partly replacive of the detrital silicates and prior cements, but are predominantly pore-filling. The final diagenetic event, prior to later dyke-induced hydrothermal alteration, is the growth of pore-bridging fibrous illite. The intrusion of a dyke in Stephanian times resulted in chlorite development as a result of hydrothermal alteration. The distribution of the diagenetic phases can

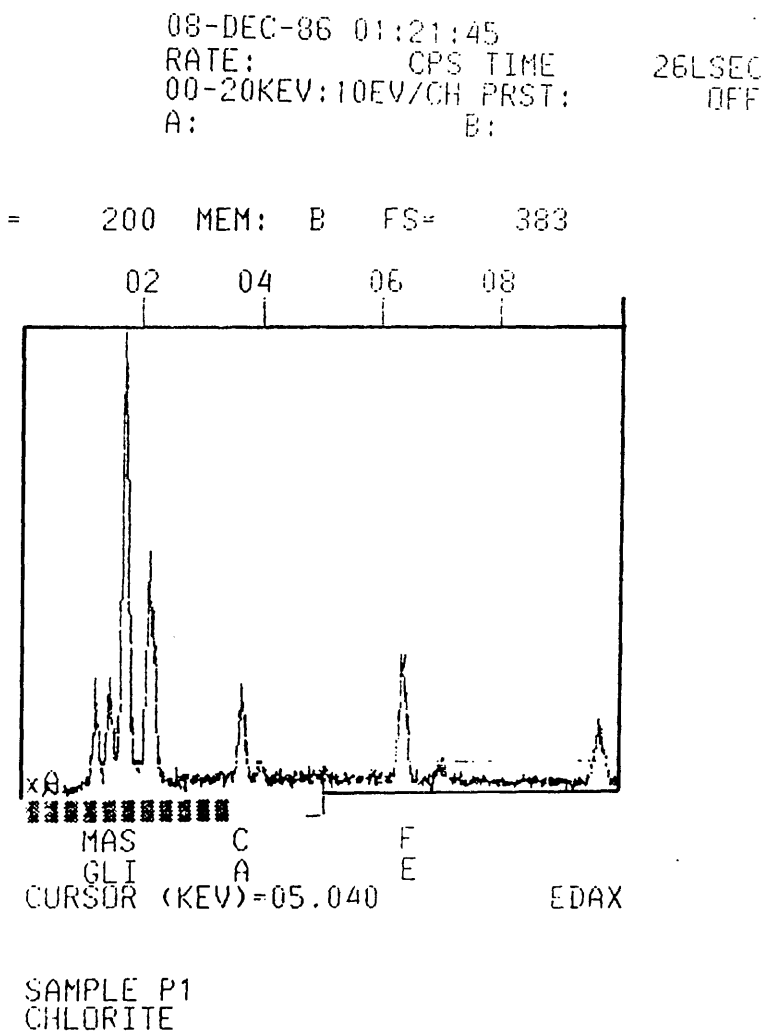


FIGURE 3.5 EDAX SPECTRA OF FE-RICH CHLORITE

PLATE 3.31 S.E.M. PHOTOGRAPH OF HONEYCOMB OR CELL-STRUCTURE CHLORITE (CHL) FORMED BY THE INTERSECTION OF CHLORITE PLATELETS (P 2.)

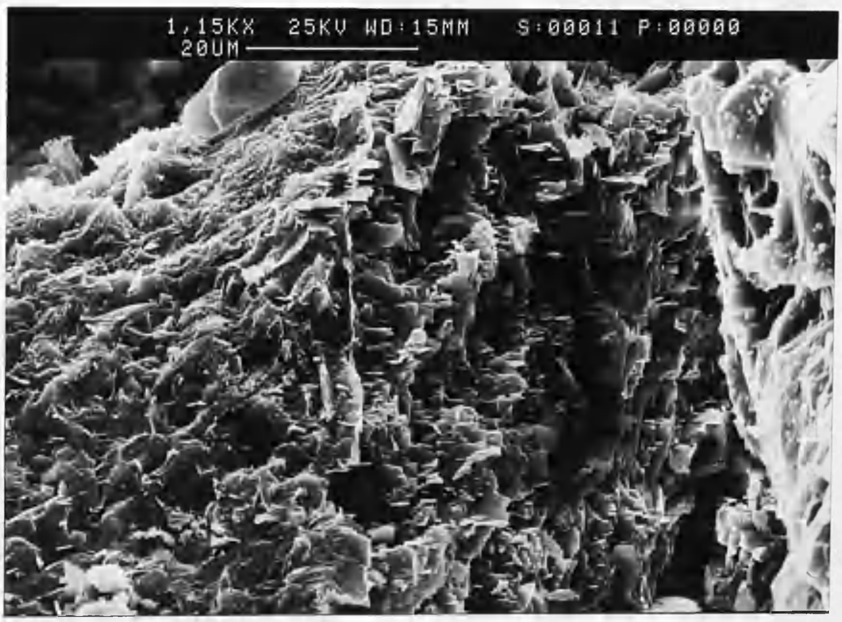
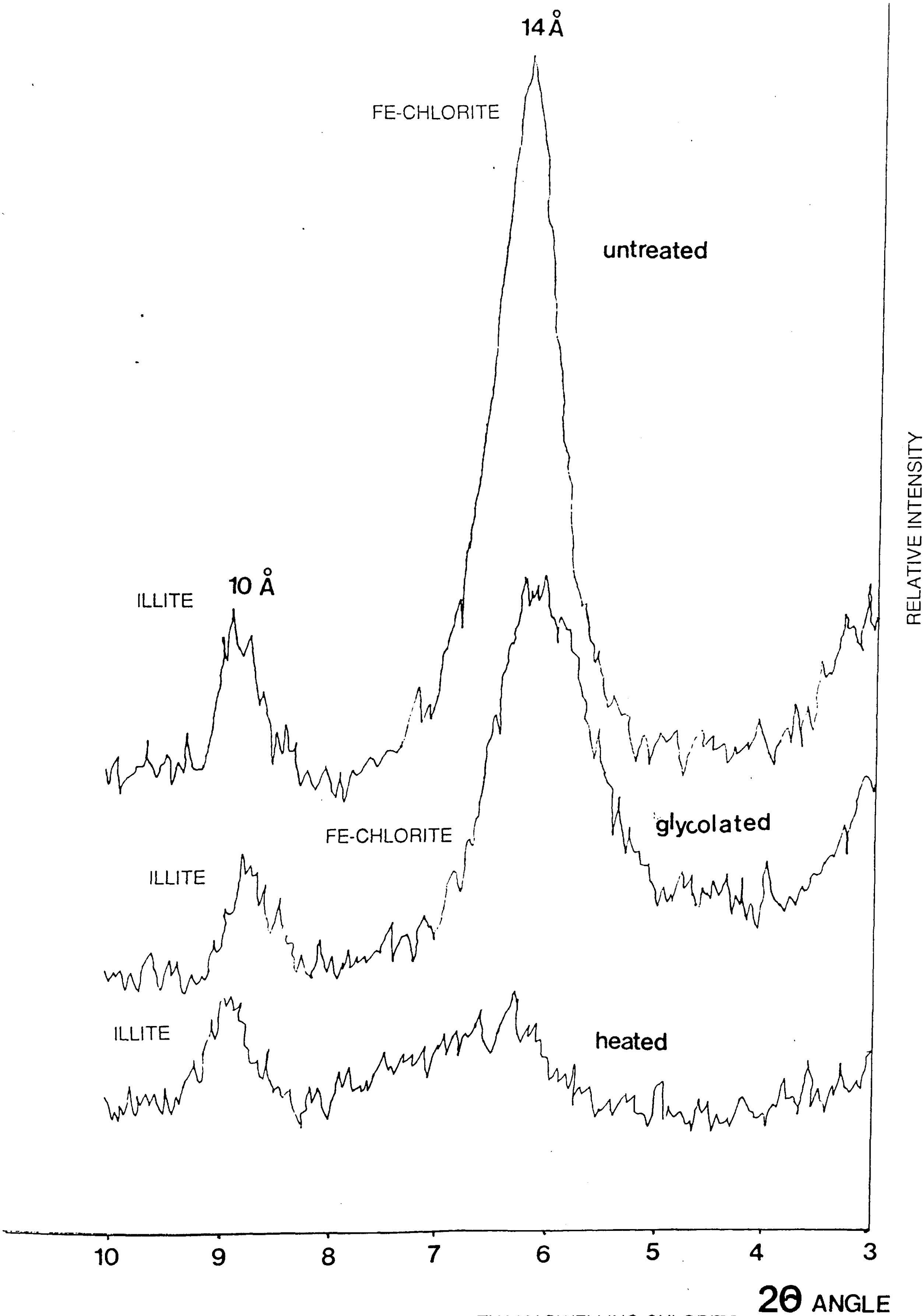


PLATE 3.32 S.E.M. PHOTOGRAPH OF CHLORITISED BIOTITE DUE TO LOCALISED DYKE HYDROTHERMAL ALTERATION (P 2.)



X-RAY DIFFRACTOGRAMS OF FE-RICH PARTIALLY SWELLING CHLORITE

FIGURE 3.6

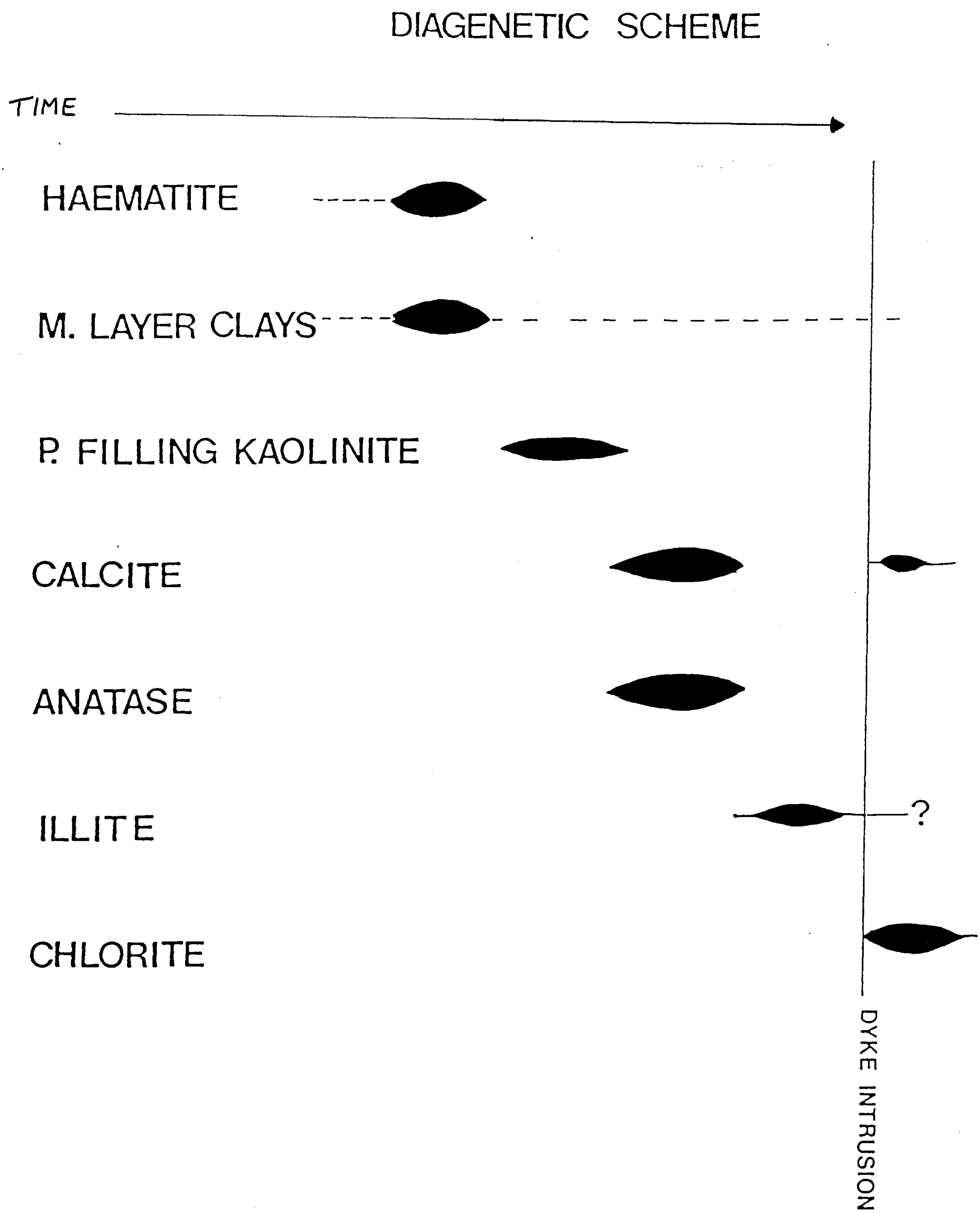


FIGURE 3.7 DIAGENETIC SEQUENCE FOR THE CROSSGATES SAND BODY

GENERALISED DIAGENETIC SEQUENCE

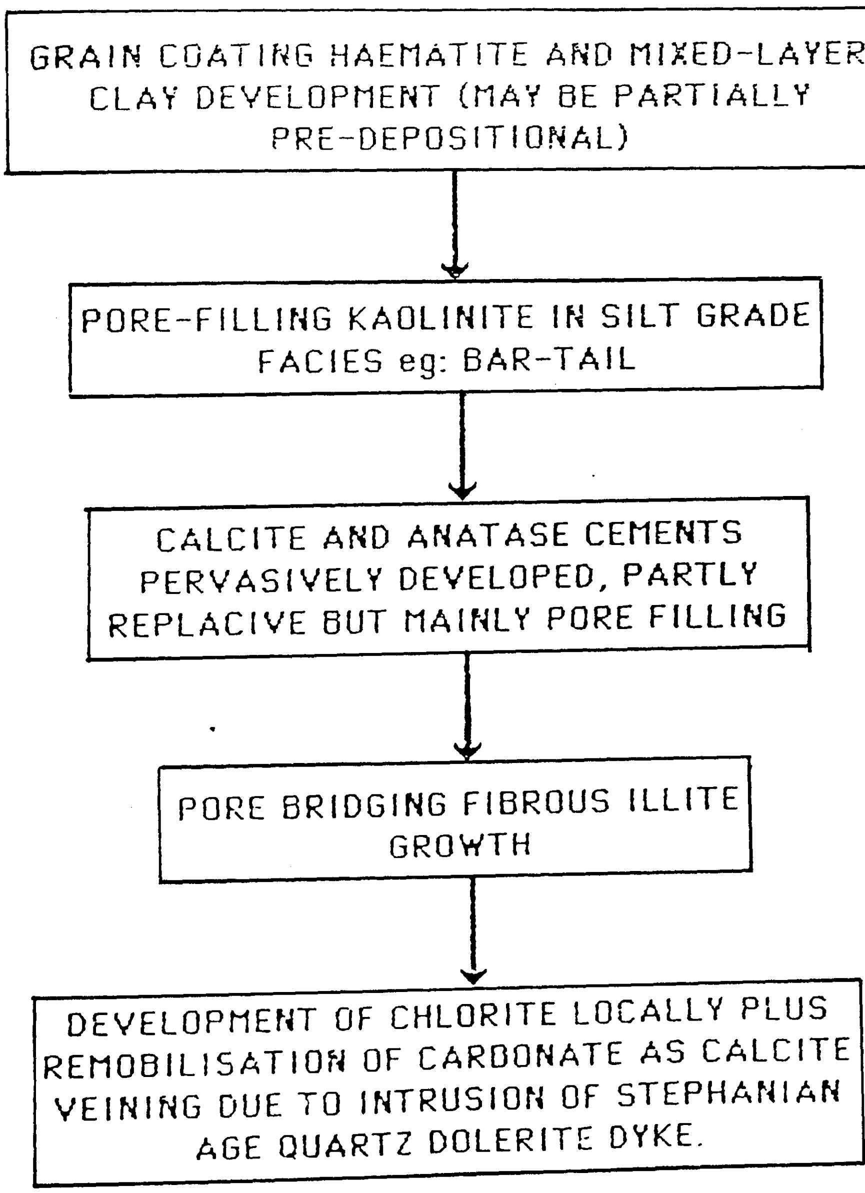


FIGURE 3.8 GENERALISED DIAGENETIC SEQUENCE OF EVENTS FOR THE CROSSGATES SAND BODY

also be summarised as follows and in Table 3.1.

BAR -TAIL

High interstitial clay content provides an effective baffle to the pore fluid circulation. Porosity and permeability are low . Diagenesis is restricted to the the development of mixed- layer clays and haematite. Both mixed-layer clays and haematite are present in small amounts as detrital components.

MID- BAR

Higher permeability in this region allows the movement of (bi)carbonate and Ti-bearing fluids through the facies, and pervasive carbonate and anatase cements were subsequently developed. These cements have partly replaced some of the detrital silicate component and prior cements. Early grain-coating haematite was re-distributed within the carbonate cement, as is suggested by disruption of the grain coat by later pore fluid. Pore space is effectively sealed and there is little evidence of any development of secondary porosity.

BAR- HEAD

Originally the most porous of the facies, the porosity has now been occluded by a sparry, non- ferroan, calcite cement which pervades the facies. Often the detrital grains are observed to 'float' in the calcite cement. Mixed-layer clay content is low and haematite is poorly developed.

CREVASSE SPLAY / OVERBANK SEDIMENTS

Low original porosity and permeability were observed; and calcitic cement is only occassionaly developed. Detrital mixed layer clays and iron oxides predominate.

IGNEOUS INTRUSION

Within the samples adjacent to the dyke intrusion, i.e. those of the Crevasse Splay / Overbank and Bar-Tail facies the diagenetic history of the sediments has been further modified by the thermal imprint of a Stephanian dyke. This intrusion has resulted in the chloritisation of ferromagnesian minerals and possible further localised illitisation. Carbonate re-distribution by hydrothermal activity has also taken place.

CHAPTER FOUR <u>STABLE ISOTOPES</u>

4.1 CARBON AND OXYGEN ISOTOPES

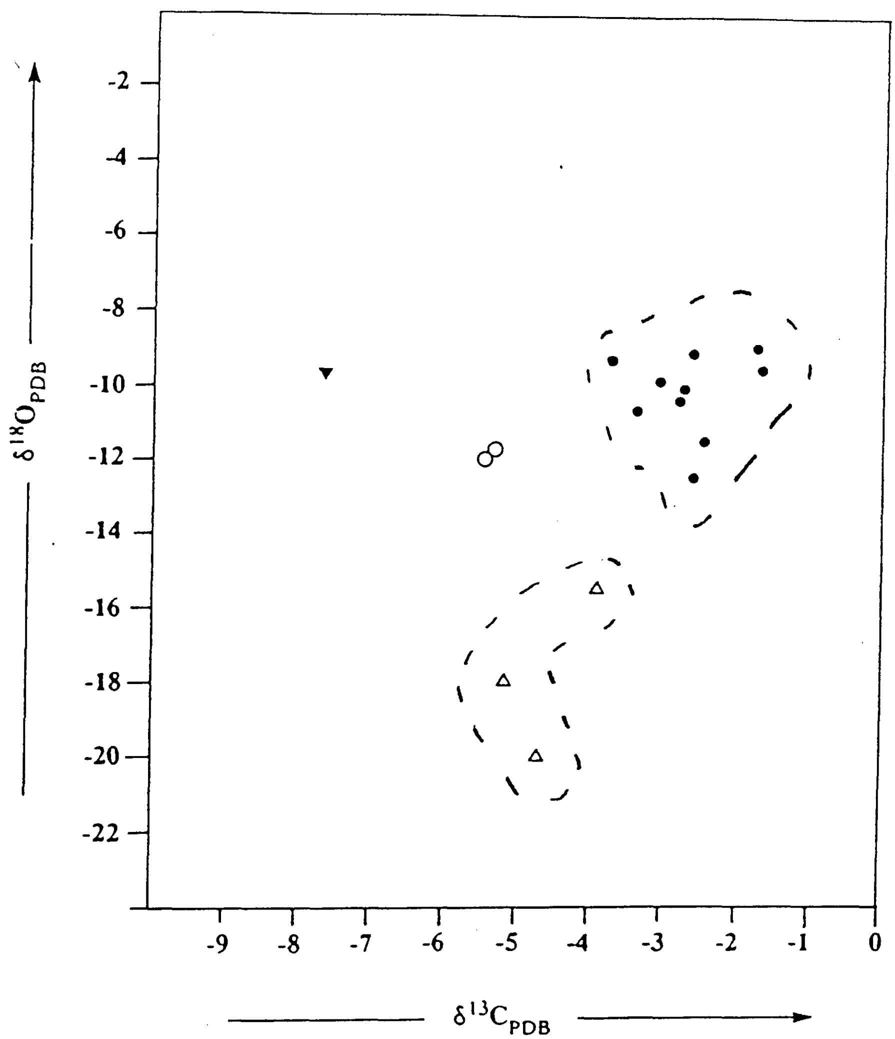
Carbon and oxygen isotope data can be used to provide valuable information on the paragenesis of carbonate minerals and cements. The ratio of ^{13}C / ^{12}C is dependant on the carbon source. Therefore the $\delta^{13}C$ composition of the carbonate can be used to indicate the possible source of the carbon available during the precipitation of the carbonate. The ratio of ^{18}O / ^{16}O is dependent on both the isotopic composition of the fluid from which the fluid precipitated and the temperature of that precipitation, (Epstein, 1959)

$$T^{o}C = 16.9 - 4.21 (\delta^{18}O^{c}_{PDB} - \delta^{18}O^{w}_{SMOW}) + 0.14 (\delta^{18}O^{c}_{PDB} - \delta^{18}O^{w}_{SMOW})^2$$

Therefore the isotopic composition of the carbonate may be used to determine the temperature ofprecipitation, or the fluid compsition if one variable is known. In this study, $\delta^{18}O$ data are calculated relative to PDB.

4.2 ANALYTICAL TECHNIQUES

Following the method outlined by M^c^Crea (1950), samples to be analysed were reacted with 5ml. of 100% phosphoric acid in a reaction vessel. The acid was degassed, and the vessel evacuated and allowed to equilibrate at 25^{o}C prior to reaction. After each sample had been reacted for 3 hours, an aliquot of CO_2 representing the calcite fraction was collected. The collected CO_2 gas was purified in a vacuum line, initially using a solid CO_2 (dry ice) / acetone slush trap to remove any water vapour. The sample of CO_2 gas was frozen using liquid nitrogen, and any non-condensable gases present were removed. The yield of CO_2 was then determined using a manometer, and the dried and purified CO_2 analysed in a VG SIRA 10 mass spectrometer.



Key:

- ▼ Stanley limestone
- ○ Pedogenic carbonate
- △ Samples affected by the dyke
- • Early precipitation of carbonate cement

FIGURE 4.1 PLOT OF $\delta^{13}C$ AGAINST $\delta^{18}O$ FOR CALCITE CEMENTS

All data were calculated relative to PDB and SMOW . Precision of the data was plus or minus 0.1‰ (1σ) or better, and the NBS 19 Carbonate Standard gave $\delta^{13}C$ = + 1. 96‰ (PDB), and $\delta^{18}O$ = - 2.19‰ (PDB). The analyses were carried out at the Isotope Geology Unit, S.U.R.R.C., East Kilbride.

4.3 ANALYSES

15 carbon and oxygen isotope analyses were carried out on the carbonate cement of samples from the various bar facies. The samples were chosen in an attempt to give three-dimensional coverage of the structure enabling modelling of the fluid flow to be attempted. The samples were then analysed using the method outlined above.

All sedimentary facies in the bar were analysed including the Crevasse Splay / Overbank deposits. A sample of pedogenic carbonate from the overlying Stanley Limestone (Campsie Formation) was also analysed, as were two samples of core from a BGS borehole at Bogle Bridge, Perth. These samples consisted of carbonate nodules within calcretised sediments of the Garvock Group. The data are presented below and in figure.4.1.

4.4 RESULTS

The carbon and oxygen isotope analyses obtained can firstly be divided into two distinct populations : those samples which reflect the effects of a Carboniferous igneous intrusion , and those samples whose isotopic signatures were unaffected by the thermal event (figure 4.1).

Samples from the Crevasse Splay ; Overbank facies and the Mid-Bar and Bar-Head calcite cements show little variation in their $\delta^{13}C$ and $\delta^{18}O$ values e.g. (Table 4.1)

TABLE 4.1

FACIES	$\delta^{13}C_{PDB}$‰	$\delta^{18}O_{PDB}$‰
Mid-Bar	- 1.70	-9.53

	- 2.77	- 10 .12
Bar-Head	- 3.40	- 10 .62
	- 2.50	- 11.47
	- 3.73	- 9.38
Crevasse Splay / Overbank	- 3.01	- 9.82
	-2.61	- 12.44
	- 2.61	- 9.19

The above samples can be seen to occupy a narrow range of both carbon and oxygen isotopic compositions. $\delta^{13}C$ values range from -1 to - 4 ‰ and $\delta^{18}O$ range from - 9 to - 12‰. These samples represent the the 'normal ' isotopic signatures for the bar sediments without any thermal influence from the Carboniferous dyke. By implication, these values represent the isotopic signature of the cement at the time of precipitation in the Devonian.

Samples from the Bar-Tail facies show carbon and oxygen isotopic compositons which reflect the influence of the Carboniferous dyke on the sediments in this facies. Some of the samples can clearly be seen to have been affected by the dyke (figure 4.1), while other samples from within the same facies show no such effects and have carbon and oxygen isotopic ratios which lie within the 'normal' isotopic range for the sediment e.g. (Table 4.2)

TABLE 4.2

FACIES	$\delta^{13}C_{PDB}$‰	$\delta^{18}O_{PDB}$‰	Affected by the dyke ?
Bar-Tail	- 1.75	- 9. 00	no
Bar-Tail	- 2.79	- 10.35	no
Bar-Tail	- 4.00	- 15.50	yes

Bar-Tail	- 5.12	- 17.91	yes
Bar-Tail	- 4.72	- 19. 95	yes

Those samples which have been affected by the dyke have more negative $\delta^{13}C$ and $\delta^{18}O$ values. This correlates with the positon of the samples in relation to the dyke, the samples which show 'resetting' of the isotopic values are located within 10metres of the dyke.The 'resetting' of the isotopic values therefore most likely resulted from the addition and / or passage of hydrothermal fluids, with subsequent solution and re-precipitation of the earlier carbonate cement, with significant addition of (bi)carbonate to the hydrothermal solution and so carbon mixing took place. The approximate thermal aureole of the dyke can thus be calculated on the basis of the stable isotope data, since the effects of the intrusion can clearly be traced isotopically, and the resultant boundary between dyke- affected and non dyke-affected sediments is clearly marked. From the isotopic data it would appear that the effective thermal aureole of the Carboniferous dyke extends to a width of less than 10m. This distance for the thermal aureole compares favourably with estimates from petrographic studies, where petrographically the influence of the thermal aureole on the mineralogy of the sediments such as 'baking', dies out after 10 metres distance from the edge of the dyke.

4.5 SOURCE OF THE CARBON

Overall, the similarity of the carbon isotopic compositions between the different bar facies, of - 1‰ to - 4‰ for those samples without the dyke 'overprint' (figure 4.1), suggests a common origin or source for the carbonate cement which pervades the sediments. The calcite cement in these samples therefore retains the isotopic signature of the pore fluid from which it precipitated. This pore fluid will most likely represent a degree of homogenization of isotopic signatures from several different sources. There are significant variations in the cement $\delta^{13}C$ and $\delta^{18}O$ values, so presumably there was not total homogenisation but some degree of local control. A possible constraint on the origin of the carbon source would be the presence of impermeable bounding surfaces formed by the overlying impermeable mudstone sequence of the Cromlix Formation and the underlying lavas of the Ochil Volcanic Formation. This would suggest an intra-formational source for the carbon.

In an attempt to indicate possible source or sources for the carbon component in the calcite cement of these sediments, samples of other local carbonate rich sediments were analysed. These were a sample of a pedogenic calcite from the overlying Stanley Limestone (Campsie Formation), and two pedogenic calcite nodules from some calcretised sediments of the Garvock Group - the latter samples were obtained from a borehole at Bogle Bridge , Perth. The samples when analysed yielded the following results (Table 4.3)

TABLE 4.3

	$\delta^{13}C_{PDB}$‰	$\delta^{18}O_{PDB}$‰
Stanley Limestone	- 7.64	- 9.46
Garvock Group (calcretised)	- 5.44	- 11.96
	- 5.40	- 11.69

The most significant feature that can be seen from the data in Table 4.3 is that the $\delta^{13}C$ values do not overlap the range of values for the Bar facies. However the $\delta^{13}C$ values obtained for the normal bar sediments are mostly a few permil. heavier than those obtained for the associated pedogenic calcite nodules within the Garvock Group. The isotopic values for these sediments may also reflect a contribution from the Stanley Limestone. A component of the requisite cement HCO_3^-could therefore have been supplied from such sources by pore fluid re-distribution. The $\delta^{13}C$ values of the pedogenic calcite itself reflects that of soil CO_2. This soil CO_2 is in turn a mixture of atmospheric and plant- respired CO_2 (Cerling, 1984). A 'heavier' HCO^-_3 source would then also be required to explain the cement $\delta^{13}C$ values. What then are possible sources of isotopically heavy carbon ? This heavy carbon could have been supplied from dissolved bioclastics with a small input from CO_2 derived from oxidised organic matter. Hovever there is no evidence of bioclastic material in the bar sediments, and so it is assumed that any contribution did occur from this source, it would have been relatively minor. Methanogenic processes such as decarboxylation resulting from the break-down of organic material within the bar sediments and associated flood - plain sediments themselves could also have contributed to the overall carbon source. The amount derived from this souce is dfficult to assess, but is unlikely to have been of much influence as these sediments are essentially barren red beds. Another possible mechanism which could produce an isotopically 'heavier' carbon source may have been the fractionation / interaction between surface water for example playa lakes and pools on the Devonian flood plains, and atmospheric CO_2. This could have led to the formation of a 'heavier ' HCO^-_3 source, which was then subsequently incorporated into meteoric waters.

It therefore can be seen that the source of the carbon component in the calcite cement is not a single source, but more likely a series of sources with different isotopic signatures. These different carbon sources have been incorporated into the pore fluid and precipitated as a cement with its own distinctive isotopic signature. There is no petrographic or field evidence within these sediments that the cement is the result *in-situ* calcretization as has been postulated for Garvock Group sediments on the east coast of Scotland (Saigal, 1985; Saigal and Walton, 1988), with the calcite cements being of a primary pedological origin. The isotopic evidence would appear to indicate a multi-source origin for the calcite cements in these Crossgates sediments with possible contributions from both the pedogenic carbonate of the overlying Stanley Limestone (Campsie Formation) and the pedogenic carbonate nodules which occur within the Garvock Group, but with a major component of heavier $\delta^{13}C$.

4.6 PRECIPITATION OF THE CARBONATE

Wtih the exception of the dyke- affected cements, all the calcite $\delta^{18}O$ values in Tables 4.1

and 4.2. are restricted to a relatively narrow range range with an oxygen isotopic composition of - 9 to - 12 ‰. Although formational mechanisms are different these calcites are all likely to have been precipitated from Lower Devonian meteoric waters for which Fallick *et al.* , (1985) estimated a $\delta^{18}O$ value of ca. - 5‰ SMOW.

Using the equation -

$$T^{o}C = 16.9 - 4.21 (\delta^{18}O^{c}_{PDB} - \delta^{18}O^{w}_{SMOW}) + (\delta^{18}O^{c}_{PDB} - \delta^{18}O^{w}_{SMOW})^2$$

(Epstein,1959)

It is possible to derive the temperature of precipitation of the bar calcite cements (fig 4.2). The oxygen isotopic compositons for the samples yield estimated precipitation temperatures for the bar cements of 35 to 50 ^{o}C, which are consistent with petrographic and calcite abundance data for formation prior to significant burial (i.e. $\leq$ 1.5 km.).

4.7 HYDROTHERMAL ALTERATION

During the late Silesian (Stephanian) tectonism in the Midland Valley led to the intrusion of a suite of tholeiitic dykes and sills along east - west extensional fracture zones. A dyke of this suite penetrated the sedimentary sequence in the Bar-Tail facies at Crossgates, and this resulted in the localised hydrothermal alteration of adjacent sediments. Stable isotope and petrographic data indicate that remobilisation of the calcite cement has occured, since both the carbon and oxgen isotopic compositions of cements (Table 4.4) in the affected sediments are considerably different from those obtained in sediments unaffected by the intrusion of the dyke. The $\delta^{13}C$ values in the thermally affected sediments are however related to those of the unaffected sediments, reflecting a Garvock Group / Stanley Limestone (bi)carbonate / carbonate component in the hydrothermal waters as would be consistent with remobilisation at higher temperatures. The $\delta^{18}O$ values can be seen to correlate with increasing distance from the dyke, and are also consistent with remobilisation at higher temperatures. The $\delta^{18}O$ values of the hydrothermally- altered sediments show an increasing

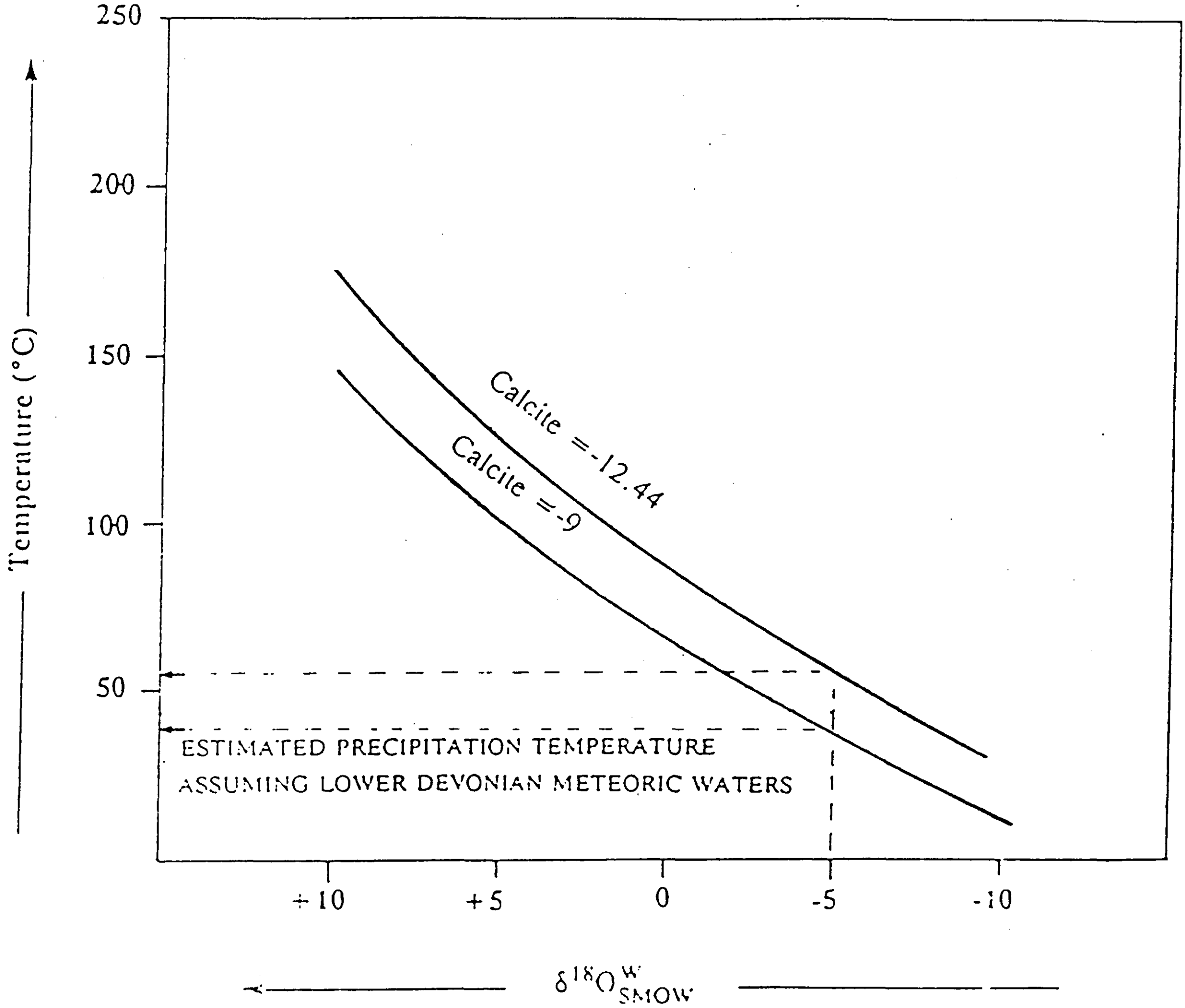


FIGURE 4.2 EQUILIBRIUM RELATIONSHIP BETWEEN $\delta^{18}O$ OF WATER, $\delta^{18}O$ OF MINERAL AND TEMPERATURE

component of magmatic / hydrothermal type waters with a $\delta^{18}O$ of ca. 6 ‰., since the $\delta^{18}O$ values become less negative closer to the dyke e.g. (Table 4.4)

TABLE 4.4.

SAMPLE	$\delta^{13}C_{PDB}$‰	$\delta^{18}O_{PDB}$‰	DISTANCE FROM DYKE
P1.	- 4.00	- 15.50	0.1m.
P2.	- 5.19	- 17.91	1.1m.
P3.	- 4.72	- 19.95	4.1m.

Such evidence may well be consistent with the addition of hydrothermal or magmatic waters at this time, and evidence of such hydrothermal effects are further provided by the petrography of these sediments. The petrograph ,ic data cited in Chapter three are consistent with an episode of calcite remobilisation with calcite veining strongly developed in this region. These calicite veins occur as 2 - 5 mm. thread-like structures which originate in the sediment body and are 'injected' into the dyke. These veins post-date the earlier authigenic calcite cement since they frequently cross-cut areas of earlier cement.The sediments adjacent to the dyke contact also show marked 'baking'. The margins of the dyke itself show slight degrees of carbonation. Feldspar phenocrysts within the contact zone of the dyke have been pseudomorphed by calcite. The minor formation of illite may have continued in the Bar-Tail facies after the intrusion of the dyke due to the hydrothermal alteration, but its main phase of development was probably pre-dyke emplacement. The distribution of authigenic chlorite is restricted to the sediments adjacent to the dyke, and its relative abundance can be seen to decrease away from the dyke (Table 3.1.). Therefore this diagenetic mineral phase is thought to arise directly from the hydrothermal alteration of ferromagnesian minerals e.g. chloritisation of biotite in the sediments adjacent to the intrusion.Therefore the intrusion of the dyke has resulted in considerable localised hydrothermal processes occurring in the adjacent sediments which can be identified in both the stable isotope data and in the petrographic data.

CHAPTER FIVE MODELLING THE DIAGENETIC ZONATION IN THE CROSSGATES SEQUENCE.

In modelling the diagenesis of a body of sediment such as the Crossgates bar, an understanding of the the sand body geometry must be obtained in order to explain the observed diagenetic features. In this case, the three - dimensional geometry of the body was well constrained. This has permitted the detailed examination and mapping of the structures and diagenetic zones within the bar. As porosity, and more importantly, the permeability controls the fluid flux within the sand body, any fluctuation or variation in the permeability of the sediments will have an effect on the diagenesis of that body. It appears therefore, that there is a distinct relationship between detrital and authigenic clay content and the permeability of the sediments. This in turn affects the amount of fluid throughput which can occur in the sediment sequence. Such a relationship can be demonstrated to exist within the Crossgates sediments i.e., - if the clay content in the sediment is high as in the siltier grade facies, then the resulting fluid throughput will be low due to decreased permeability. This occurs due to the fact that although clay coatings may occupy only a small volume of pore space, their diagenetic development can restrict the diameter of pore- throats thereby impeding and restricting fluid motion. These grain coatings therefore constitute effective permeability barriers within the bar facies, restricting the movement of pore fluids, and the affected sediment zones act essentially as restricted systems in terms of pore fluid movement. The diagenetic history of such zones reflects this with authigenic mineral growth restricted to iron oxides and mixed-layer clay development. Clay content can be demonstrated to have controlled the diagenesis of the Bar-Tail facies in this fashion. If the clay content is low, then the fluid throughput will be high and large volumes of pore fluid can circulate through essentially 'clean' sands, with the accompanying development of pore water derived cements. The flushing of large volumes of pore water through these sandstones is indicated by numerous lines of evidence which include the extensive aggresive dissolution of chemically unstable materials such as clay clasts, micas and felspars, and prior diagenetic cements. Pore water derived cements were then subsequently precipitated. The diagenetic history of the Bar-Head facies is thought to have been influenced by this relationship.

The above mechanism is thought to be responsible for the the formation of the distinct diagenetic zones, and in particular the distribution of the carbonate cement. The original depositional facies correlate well with the observed zonation and as such are thought to be the primary control on the subsequent diagenesis of the sequence. This zonation results in considerable inhomogeneity of reservoir characteristics.within the bar facies, and indicates that such sequences should not be regarded as wholly homogenous sequences, since there may be in close spacial association, related sediments of highly contrasted porosities and permeabilities. Such horizontal and vertical porosity and permeability anisotropies reflect the influences of depositional facies, sand body geometry and fluid flow and diagenetic hist ories. Therefore the reservoir characteristics of such an alluvial system may be highly varaible with resulting implications for oil / gas recovery and production.

Primary pedological calcrete formation in the sediment as suggested by Saigal, (1985) and Saigal and Walton, (1988) to be the source of the carbonate cement in the Garvock group in the east of Scotland, is not thought to be a factor in the diagenesis of this sand body. The sand bar shows no field evidence of calcretisation, - no vertical stratafication of the carbonate cement is indicated, as would be consistent with the downwards calretisation of the sand bar. The cement is homogenous throughout the sequence. Stable isotope data also indicate that the cement is unlikely to be as the result of primary pedological processes, but appears to represent precipitation from a pore fluid derived from a mixture of isotopic sources.

The compsition of this pore fluid indicates not only appreciable enrichment in (bi)carbonate but also in titanium, as anatase is co- precipitated with calcite. In order to precipitate the the amount of authigenic anatase (TiO_2) present within the sediments, a considerable source of titanium must be available. It is unlikely that the requisite amount of titanium could be derived from the *in-situ* degradation of igneous-derived material in the sedimentary sequence since such material does not exist in abundance in the sediments. Therefore the titanium must have been derived from another source to enable the pore fluid to become sufficently enriched in titanium to account for its precipitation as anatase. The most obvious source for this enrichment is the underlying volcanic sequence of Lower Old Red Sandstone lavas of the Ochil Volcanic Formation. The Garvock Group lies conformably on these lavas. Titanium may have been scavenged from the sediment- lava interface due to alteration of the igneous material.

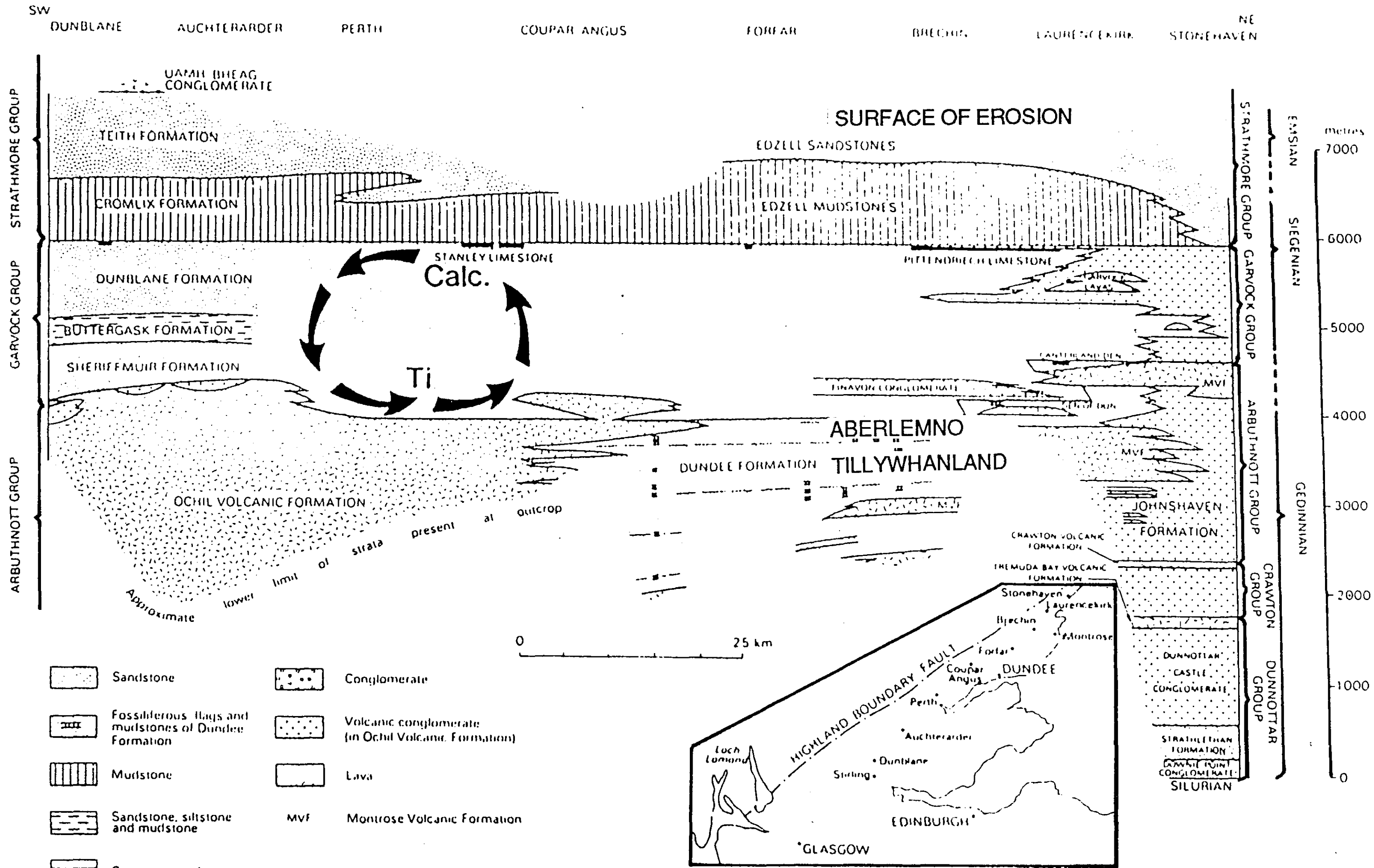
Such a mechanism would involve net transport of titanium in pore water from the Ochil Volcanic Formation through the Garvock Group. A possible mechanism for such meteoric flushing is that described by Wood and Hewett, (1982; 1984) and in subsequent papers by Davis *et al.*, (1985), and Haszeldine *et al.*, (1984). Wood and Hewett, (1982) postulated that the free convection of pore fluids can result in the mass transfer of mineral phases within sandstone reservoirs with a geothermal gradient of as low as $25^{o}C$ / km., and it is thought that such a mechanism was responsible for the transport of both (bi)carbonate and titanium from their original source areas to the areas of precipitation.

Fluid flow within the Garvock Group sediments (figure 5.1) is controlled vertically by the overlying impermeable mudstone sequence of the Cromlix Formation, which outcrops on the south east limb of the Strathmore Syncline. This succession conformably overlies the Garvock Group in the area, and provides an impermeable ' cap ' or ' seal ' to the Garvock Group. The lower surface of the ' reservoir ' (in this case the Garvock Group) is bounded by the underlying impermeable lavas of the Ochil Volcanic Formation. Therefore the 'reservoir ' in which fluid circulation took place may be constrained, and it is likely that fluid circulation was limited to the Garvock Group.

The timing of the fluid circulation may also be constrained by a number of factors.

1. - Preservation of the original pore space geometry, now infilled by carbonate, with only minor degrees of compaction evident.
2. - Precipitation of the carbonate cement at 35 - $50^{o}C$, indicating shallow burial at the time of precipitation.
3. - Re - mobilisation of the carbonate cement by the Stephanian dyke indicating that cementation had occurred by the Late Carboniferous.

Sedimentation in the area ceased with the onset of tectonic activity, at the end of the Lower



(Adapted from Armstrong & Paterson, 1970)

FIGURE 5.1 POSSIBLE FLUID FLOW PATHS WITHIN THE GARVOCK GROUP SEDIMENTS

Devonian during which north easterly trending folding occurred, leading to the development of the Strathmore Syncline and associated Sidlaw Anticline. The youngest rocks of the Strathmore syncline, the Strathmore Group, are of late Siegennian age, (House *et al.*, 1977). So the deformation responsible for the Middle Devonian unconformity in Scotland, may well have begun or been initiated in the Lower Devonian. It is likely that the early circulation of the pore fluids and subsequent cementation of the bar sediments also commenced at this time i.e. late Lower Devonian.

Fluid flow was probably initiated by this folding event and the fluid circulation pattern is approximately indicated by the presence of (bi)carbonate from the overlying calcretised sequences, and the Stanley Limestone and the scavenging of titanium from the underlying lavas of the Ochil Volcanic Formation.

In geological structures and environments the geometry of the reservoir body controls the flow geometry encountered in the reservoir. If the reservoir is no longer an essentially planar structure, due to the effects of deformation, then the flow geometry will be altered accordingly. In the case of the Garvock Group, which is taken to be the theoretical ' reservoir ', the reservoir has been defomed into a synclinal structure. Within this synclinal structure, torus- type cells (figure 5.2) may well have existed, formed by temperature variations within the structure itself . these temperature variations may have been enhanced by the presence of a still cooling volcanic pile i.e. the Ochil Volcanic Formation, beneath the sediments. In general though the geometry and structure of the reservoir exerts the dominant influence on the subsequent geometry and distribution of convection cells which develop within it. In synclinal structures,' hot ' fluid within the convection cell ascends along the base of the resrvoir and rises at the crests, while ' cooler ' fluid flows down along the top of the reservoir and returns to the the bottom of the cell at the synclinal trough.

As a fluid particle moves around a free convection cell, it alternatively encounters regions of ' low ' and ' high' temperature as the particle passes along a temperature gradient. This effects a net transport of heat from warmer regions to cooler areas. If the fluid also carries dissolved solids which have a temperature dependant solubility then a net transport of material will also occur. For minerals such as quartz whose solubilty in water increases with temperature (Helgeson, 1969) and is therefore regarded as a prograde mineral, quartz will be leached from areas which were hotter and re -

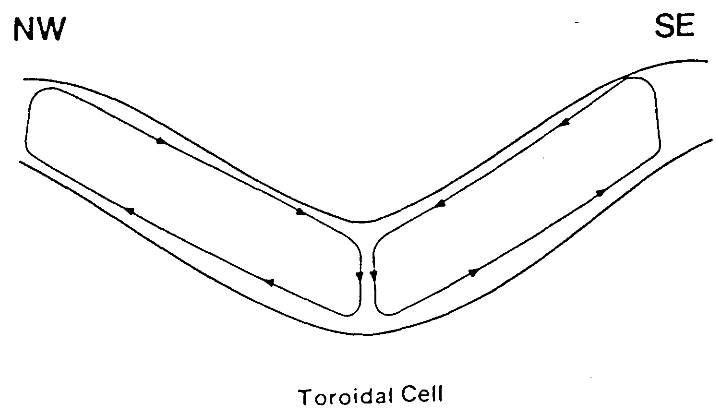


FIGURE 5.2 TORUS-TYPE CELL STRUCTURE SHOWING FLUID FLOW WITHIN THE STRATHMORE SYNCLINE-SIDLAW ANTICLINE REGION

precipitated in areas where the convecting fluids were cooled. Therefore a convecting fluid will move a prograde mineral such as quartz from ' hot ' sources to 'cold ' sinks. For minerals such as calcite, which shows retrograde solubility (Helgeson, 1969; Wood, 1986; Wood and Hewett, 1984, 1986), the precipitation / dissolution pattern will be reversed i.e., calcite will dissolve in the cooler regions and be precipitated in the hotter regions. In effect calcite would move from a ' cold ' source area to a ' hot ' sink and therefore the net effect in the case of the Garvock Group would be a downwards transport of calcite. This would agree with the suggested source area for the carbonate cement as the Campsie Formation lies stratigraphically above the Scone Formation, in which the Crossgates sand body occurs.

Within the Garvock Group, carbonate would be dissolved from the overlying Stanley Limestone of the Campsie Formation and possibly also from other stratigraphically higher calcretised sediments within the Group, resulting in the mixing of carbon sources indicated by the Stable Isotope evidence. Within this convection cell where fluid circulation would be bounded at its base by a volcanic suite, fluid would circulate along the sediment - lava interface scouring titanium from the the uppermost lavas. Exposed lava sequences in the Ochil Hills show alteration at the sediment - lava contact, indicating that some degree of interaction between the sediment and the lavas has occurred. Titanium acquired in this manner would then be incorporated into the pore fluid and transported upwards following the flow path of the toroidal cell.

Although arguments have been raised regarding the validity of such convection cells in larger scale sedimentary basins (Bjørlykke *et. al.*, 1988), such a mechanism may be implied in the Crossgates sediments. A convection cell system does represent a possible for fluid circulation which would allow the apparent mixing of Ti and CO_2- bearing pore fluids, which subsequently co - precipitated to form the pervasive anatase and calcite cements observed in the bar sediments.

CHAPTER SIX CONCLUSIONS

The recognition and investigation of diagenetic zones within petroleum reservoirs can lead to important implications regarding the 'quality ' of the reservoir in terms of oil and gas recovery. Hydrocarbon reservoirs should not be regarded as homogeneous bodies, but as highly complex and heterogeneous structures, with varying porosity / permeability zones. These zones of often highly contrasted porositites and permeabilities reflect the influence of depositional facies, sand body geometry and fluid flow, and diagenetic histories.

The onshore succession of the Lower Devonian Garvock Group at Crossgates provided an excellent opportunity in which to investigate possible diagenetic zonation within a sediment body. The locality had suffered only minimal surface weathering and erosion, and the unusually large scale of the structure allowed detailed investigation of the different component lithofacies within the structure. This permitted diagenetic zones within the sediment body to be clearly recognised.

Within the Crossgates sediments, a series of distinct porosity / permeability zones could be recognised. These zones of anisotropy closely correspond to the sedimentary facies and, as such most likely arise from the effects of hydraulic sorting on the grain size, detrital composition and sedimentary textures of the individual facies components of the sand body. This has led to the marked porosity / permeability anisotropy seen within the different facies.

This porosity / permeability anisotropy has had a profound effect on the diagenesis of the Crossgates sequence, and can be classed as one of the major influences on the diagenetic history of the sequence. The paragenetic sequence for these sediments can be briefly summarised as follows : Initially, grain-coating haematite and mixed layer clays were developed [mostly as a result of diagenetic processes, but some formation may be partially pre - depositional). Subsequent pore - filling kaolinite and associated minor quartz overgrowths are prominent in the siltier - grade facies, such as the Bar - Tail. The development of the diagenetic minerals is quite markedly preferential to certain facies and is related to both the detrital compositon of the facies and the porosity / permeability charactereristics of that particular facies. Post - kaolinite formation, there occurs a phase of pervasive carbonate and anatase. Although pervasive throughout the sequence, the carbonate is best developed in the most porous facies of the bar, for example in the bar -head where it occurs as a pore-filling cement. Such a distribution pattern for the carbonate and anatase again reflects the influence of porosity and permeability anisotropies on the distributon of diagenetic minerals. The carbonate and anatase are only particularly well-developed in facies where the original porosity and permeability were high enough to allow the passage of [bi]carbonate and Ti - bearing fluids through the facies. The final diagenetic event, prior to later dyke-induced hydrothermal alteraion, is the growth of pore - bridging fibrous illite whose development is again influenced by porosity / permeability anisotropy and the original detrital mineral composition of the facies.

Within samples adjacent to the Stephanian dyke, the diagenetic history of the sediments has been modified by thermal imprint. This intrusion has resulted in the chloritisation of ferromagnesian minerals and possible further minor illitisation. Carbonate redistribution by hydrothermal activity has also taken place.

Within the Crossgates sequence, the presence and development of distinctive diagenetic zones or facies clearly correlates with the development of porosity and permeability anisotropy in the sediment body itself. The recognition of such diagenetic zones and factors influencing their formation and development is thus clearly important. By studying the distribution of such diagenetic zones in detail it may be possible to recognise diagenetic zonation within a hydrocarbon reservoir, and hence more accurately model the diagenetic features of that reservoir with the accompanying implications for oil and gas recovery.

The similarity between the carbon isotopic compositions of the carbonate pore - fluid in the bar - facies, of -1‰ to -4‰, in non-dyke-affected sediments indicates a common origin for the carbonate. Stable isotope data indicate that the carbon component has not one single source, but represents a series of sources with different isotopic signatures. These different carbon sources have been incorporated into the pore - fluid and precipitated as a cement with its own distinctive isotopic signature, with possible contributions from both the the pedogenic carbonate of the overlying Stanley Limestone (Campsie Formation) and the pedogenic carbonate nodules which occur within the Garvock Group.

The oxygen isotopic compositions for the samples indicate estimated precipitation temperatures for the bar cements of 35 to 50^{0}C, which are consistent with petrographic and abundance data for formation of the carbonate cement prior to significant burial (i.e. ≤ 1.5 km.).

Local hydrothermal alteration of the sediments adjacent to the dyke has led to the re-precipitation of carbonate in the form of veins. These veins originate in the sediments and result from the re-mobilisation of calcite with the addition of hydrothermal or magmatic waters. Associated with the intrusion is the formation of authigenic chlorite.

The apparent composition of the pore fluid suggests considerable enrichment in both (bi)carbonate and TiO_2, the former arising from the pre-existing carbonates within the group and the latter from underlying volcanic lavas of the Ochil Volcanic Formation. This suggests the possibility that large-scale fluid circulation by convection occurred within the Garvock Group and was most likely associated with the tectonism which produced the Middle Devonian unconformity. Such a mechanism would involve net transport of titanium in pore water, from the Ochil Volcanic Formation through the Garvock Group, similar to that described by Wood and Hewett, (1982; 1984), Davis *et al.*, (1985) and Haszeldine *et al.*, (1984).

Although arguments have been raised regarding the validity of such convection cells in large-scale sedimentary basins (Bjørlykke et al., 1988) and such a mechanism can only be implied, it does represent one explanation for the co-precipitation of calcite and anatase within the sediments.

The diagenetic history of the Crossgates sediments can be seen to be the result of the interaction of highly complex factors, which have both influenced and modified the diagenesis of the sequence. Implications from this study are that hydrocarbon reservoirs cannot be regarded as homogenous units, but as highly structured, anisotropic bodies. Horizontal and vertical porosity / permeabilty anisotropies in the sediment body ultimately reflect the influences of depositional facies, sand body geometry, fluid flow and diagenetic histories. Therefore the reservoir characteristics of such alluvial systems may be highly variable with resulting implications for oil and gas recovery.

Future work on this topic would include the application of these findings and techniques to actual hydrocarbon-bearing reservoirs.

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APPENDIX 1. <u>PREPARATION OF SAMPLES FOR X-RAY DIFFRACTION</u>

Samples were prepared for X.R.D. using the following method adapted from Pagan, (1980).

1) 20g of rock were carefully crushed in an a mortar and pestle, to avoid possib;e dislocation of the clay platelets.

2) The 20g of powder was then placed in a 250ml. beaker, and filled with distilled water untill 200ml. mark was attained - usually when a depth of 6cm. was reached.

3) 2.5g of sodium hexametaphosphate was then added to the solution.

4) The solution was then placed in an ultrasonic bath for 30 minutes, and stirred occasionaly to prevent sediment build up on the base of the beaker. After 30minutes the solution was removed from the bath and stirred using a side to side motion to prevent size segregation within the beaker.

5) The solution was allowed to settle for 1.5 hours - all particles greater than 2 microns are then be below the 2cm. mark. The time requred was estimated using Stokes Law of settling under gravity.

6) The top 2cm. of solution was then pipetted off using a 50ml. pipette, and placed in a 100ml. beaker . Care was taken to avoid sampling from below the 2cm. mark. The sample now contains a solution of size fraction less than or equal to 2 microns.

7) the beaker containing the solution was then transferred to a hot plate, and the solution was evaporated to approximately half its volume at a constant 80^{o} C.

8) Using a 5ml. pipette, three X.R.D. 'tiles' were prepared for each sample - a small quantity of the solution was placed on a glass slide and allowed to evaporate to dryness, this was repeated three tim to give three X.R.D. samples.

Three samples were prepared to allow for heating and Glycolation of the samples. Each sample was run as 'untreated', heated and Glycolated. The heated samples were prepared by heating in a furnace at 550^{o} C for thirty minutes, the samples were heated to verify the prescence of kaolinite which becomes amorphous at temperatures > than 500^{o}C, the peaks assigned to kaolinite at 7.15 A. and 3.57 A disappear The Glycolated samples were prepared by placing the 'tile' to be Glycolated, in a dessicator containing ethylene glycol overnight, the prescence of 'expandable' clays can be verified on expansion.The glycol vapour being absorbed by the interlayers of the clays.

Analysis of the clays was done using a Phillips X-ray Diffractometer with Goniometer attachment. identification of the clay structures was done using Thorez, (1975) and Brindley and Brown eds.,(1980)).

APPENDIX 2. PERTH SAMPLE LOCALITIES

IDENTIFICATION	DISTANCE TO DYKE	FACIES
P1	0.1m	Bar-Tail
P2	1.1m	Bar-Tail
P3	4.1m	Bar-Tail
P4	8.1m	Bar-Tail
P5a	12m	Bar-Tail
P5b	12m	Bar-Tail
P6	14m	Bar-Tail
P7	24m	Bar-Tail
P8	49m	Bar-Tail
P9	79m	Lenticle (Mid-Bar)
P10	110m	Mid-Bar
P11	110m, but vert. 4.5m from P10	Mid-Bar
P12	110m,but vert. 3m from P11	Mid-Bar
P13	160m	Mid-Bar
P14	160m, but vert. 2.25m from P13	Trough (Mid-Bar)
P15	160m, but vert 5.25m from P14	Trough (Mid-Bar)
P16	160m, but vert. 7.5m from P 15	Mid-Bar
P17	210m	Bar-Head
P18	210m, but vert. 3.25m from P17	Bar-Head
P19	260m	Bar-Head
P20	310m	Bar-Head
P21}	distances not	Crevasse Splay / Overbank

P22}	measured	Crevasse Splay / Overbank
P23}		Crevasse Splay / Overbank
P24	20cm	Crevasse Splay / Overbank
P25	1m	Crevasse Splay / Overbank
P26	1.5m	Crevasse Splay / Overbank
P27	1.5m	Crevasse Splay / Overbank