DIAGENESIS OF THE OOLITE GROUP BETWEEN BLAEN ONNEU AND PWLL DU, LOWER CARBONIFEROUS, SOUTH WALES.

by

MADELEINE JULIA RAVEN, B.Sc.

Thesis submitted to the University of Nottingham for the degree of Doctor of Philosophy, October 1983.

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ACKNOWLEDGEMENTS

Many people have been involved both in the production and the work behind this thesis. In particular I must thank Dr Tony Dickson for his guidance in the early stages of the work and for his constructive criticism of the text and Dr Max Coleman for his invaluable help, advice and guidance in the isotope analysis.

My thanks to Dr. Paul Wright for providing me with samples from the Llanelly Fm for the purpose of comparing the CL of their cements with those in the Oolite Group and for the hours of discussion we had.

Diagrams and plates could not have been produced without the expertise of David Jones who was also responsible for developing vast amounts of film for me. I must also thank the rest of the technical staff in the Department of Geology, especially Andy Swift and Walter Wilson, who kept the luminoscope running. Thanks also must go to the staff at the IGS isotope laboratory, London for their help.

While doing field work I stayed at the Red Dragon Hotel, Crickhowell. Many thanks to the management and staff of that excellent establishment for making my stays there so enjoyable.

The work was done while I was in receipt of an NERC grant. The thesis was produced with the aid of a Research and Development Grant from Robertson Research Int.

My thanks to Julie Leppard for typing the text.

ABSTRACT

The diagenetic history of the Oolite Group from Pwll du to Blaen Onneu has been unravelled. Cement types, solution events, dolomitisation, concretions and other authigenic minerals are described.

The calcite cement crystals show chemical zonation through staining but cathodoluminescence (CL) has proved the most useful method for displaying internal features of calcite crystals. CL makes it possible to trace the growth of crystals and monitor changes in crystallographic form during growth. Seven cement zones are identified using stained specimens. Each zone has a characteristic luminescence. The age of these zones relative to the exposure of the top of the Oolite Group is established. Two distinct diagenetic areas are recognised on the basis of the distribution of the cement zones.

Area 1 : the Pwll-y-cwm and Blaen Onneu Oolites in the Clydach area, in which Zones 1, 2b and 6 are present,

Area 2 : the rest of the Oolite Group, in which Zones 2a, 3, 4, 5 and 6 are present.

It is possible to correlate the cement zones of Area 2 along the outcrop for a distance of 8 km and also with cements in the overlying Llanelly Formation. Dolomitisation prevents correlation of cements in Area 1 over a distance of more than ½ km.

Using CL it is possible to identify solution surfaces, on a micron to millimetre scale, within the cements. Four solution events are identified in Area 2. Solution effects that are previously unreported are described. The presence of solution surfaces is used to illustrate the constantly changing nature of the pore waters that have affected the Oolite Group.

Carbon and oxygen stable isotope analysis of allochems and cement zones highlights the distinction between Areas 1 and 2 and are used to try and identify the nature of the pore waters affecting the Oolite Group during its diagenesis. The carbon isotopic composition of the allochems and cements pre-dating the exposure of the top of the Oolite Group is related to their distance below the exposure surface at the top of the Oolite Group and thus seems to reflect meteoric alteration. The successive cement zones do not show a progressive trend in carbon and oxygen values; however, in different samples successive cement zones do show the same pattern of changes in carbon and oxygen values. The values typical of a specific cement zone are thought to relate to the pore fluids from which it was precipitated. The pattern of changes seen in successive cement zones is explained in terms of changing pore water chemistry and isotopic composition with time. These changes occurred over an area at least the size of the study area. Very light oxygen values in veins are attributed to increased temperatures associated with deep burial.

An attempt is made to reconstruct the paleohydrology of the study area in an attempt to explain the nature and distribution of the cements.

FOREWORD

The various diagenetic events affecting the Oolite Group are discussed first in the text, i.e. cementation, solution, dolomitisation, authigenic mineral growth and concretion growth. Then an attempt is made to combine these along with carbon and oxygen stable isotope data to give an overall picture of the environments in which diagenesis within the Oolite Group was occurring and how and why these changed with time.

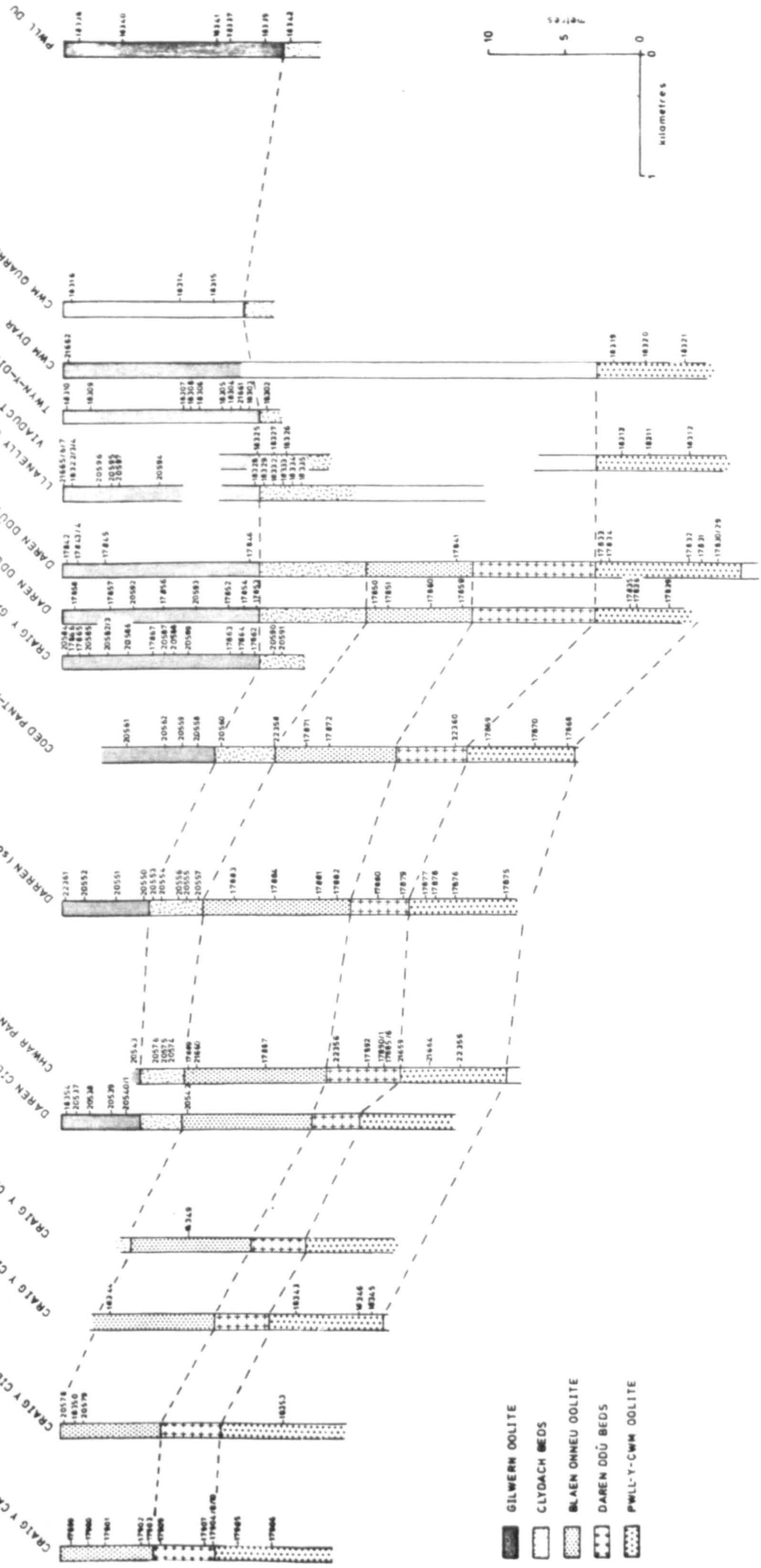
Numerous photographs are used to illustrate the various diagenetic features within the Oolite Group, especially the cements. All black and white photographs were taken using cathodoluminescence (CL) unless otherwise stated. For the conditions under which these photographs were taken see Appendix A. Scale bars are all 100 µm. unless otherwise stated.

Tables, graphs, line drawings and black and white photographs are all given 'Figure' numbers. Each 'Fig.' number consists of two parts. The first number indicates the chapter to which it is related and the second number runs consecutively through the chapter and indicates the relative position of the 'Fig.' in that chapter. Colour photographs are termed 'Plates'. The numbering system for these is the same as that described for 'Figs.'

Samples collected from the study area have been given five figure numbers. These numbers will be used later in the text when specific samples are referred to. The localities and stratigraphic levels from which the samples were collected are shown in Fig.1 .

Fig.i LOCATION OF SAMPLES IN THE STUDY AREA

Section through the study area showing the position of samples and their reference numbers.The locations of place names are shown on Fig.1/2.


PWLL DU
CWM QUARRIES
CWM DYAR
TWYN-Y-DINAS
VIADUCT
LLANELLY QUARRY
DAREN DDÛ (south)
DAREN DDÛ (north)
CRAIG Y GAER
COED PANT-Y-DAREN
DARREN (south)
CHWAR PANT-Y-RHIW
DAREN CILAU
CRAIG Y CILAU (south)
CRAIG Y CILAU (middle)
CRAIG Y CILAU (north)
CRAIG Y CASTELL
metres
10
5
0
kilometres
0
1
GILWERN OOLITE
CLYDACH BEDS
BLAEN ONNEU OOLITE
DAREN DDÛ BEDS
PWLL-Y-CWM OOLITE

CHAPTER ONE

INTRODUCTION

1.1 Background

Geological setting

The limestones, dolostones and shales of the Carboniferous Limestone in South Wales lie between the fluviatile Old Red Sandstone below and the deltaic-paralic Millstone Grit and Coal Measures above (George, 1970). It is the product of flooding of the Old Red Sandstone continent by shallow shelf seas at the beginning of the Carboniferous. This mainly carbonate sequence was deposited as a northward thinning wedge, probably up to 100 km. wide, between the deeper water shales and turbidites of the Culm Basin to the south and a land area, St. George's Land, to the north. The thickest exposed sequences are along the southern coast of Wales where it is over a 1000 m. thick. Northwards, across the syncline of the South Wales coalfield, the succession thins to less than 150 m., partly because of post-Lower Carboniferous overstep and erosion by the Millstone Grit, but mainly due to the effects of disconformities within the sequence that become more numerous towards St. George's Land. The tapering northern edge of the carbonate wedge is removed by erosion in central Wales.

The attenuated succession in the northern part of the South Wales Coalfield consists of four main divisions: the Lower Limestone Shales, the Oolite Group, the Llanelly Formation and the Dowlais Limestone. This study is concerned only with the

Oolite Group exposed between Pwll du and Blaen Onneu (Fig. 1/1 and 2). Within the field area the Oolite Group outcrops as an almost continuous string of quarries (Fig. 1/2) which lie in a north-west to south-east direction, i.e. at right angles to the shore line that existed at the time of Oolite Group deposition (Robertson & George, 1929). The good exposure means that identification and correlation along the outcrop is easy. However, the sheer nature of the quarry faces does mean that close examination of much of the rock is impossible. The extent of the field area chosen is delineated to the east by the complete dolomitisation of the Oolite Group. The western limit of the field area is taken at Blaen Onneu, for west of this locality the outcrop deteriorates in quality and identification and correlation of the beds becomes difficult.

Previous work

Accounts of the Oolite Group are given by George (1927, 1954), Robertson (1927) and Robertson & George (1929). These are concerned with the stratigraphy of the Group rather than any sedimentological or diagenetic interpretation. Detailed sedimentological studies have recently been undertaken of the Lower Limestone Shales (Burchette, 1977) and the Llanelly Formation (Wright, 1981). Wright (1981) summarises the geology of the area and discusses previous interpretations of the Lower Carboniferous in the northeast part of the S. Wales coalfield. Wright (1980, 1981, 1982) gives a comprehensive account of the nature and origin of the top of the Oolite Group, which was first described by Thomas (1953) and later by George (1954).

The dolomites of the east crop that extend into the southeast of the study area are discussed by George (1955) and Bhatt (1972, 1973, 1976).

Gill et al. (1977) determined the degree of metamorphism of the study area as part of a larger study of the South Wales coalfield. They placed the study area in 'Diagenetic Zone 1', i.e. pre-metamorphic. A maximum temperature and depth of burial was not suggested for this zone, but the temperature probably never exceeded 200°C, which is given by Winkler (1979) as the upper limit for the diagenetic zone.

Stratigraphy

The stratigraphy of the lower part of the Carboniferous Limestone of the northcrop and the development of the nomenclature of these rocks is summarised in Fig. 1/3. During the course of this study it became evident that the nomenclature of George et al. (1976) was inappropriate and it has been revised as follows:-

1. the 'Coral Bed' has been placed in the Gilwern Oolite rather than the Clydach Beds since it grades into typical Gilwern Oolite sediments;
2. the Clydach Beds are extended downwards to include any dolomites, micrites and shales above the Blaen Onneu Oolite;
3. a new name is given to the beds between the Blaen Onneu and Pwll-y-cwm Oolites. These are called the 'Daren Odu Beds';
4. the dolomite at the base of the Oolite Group is separated from the Pwll-y-cwm Oolite (as in George, 1954). This has not been named.

These revisions are identical to those proposed by Barclay (pers. comm.) However, he calls the Daren Odu Beds, of this study, the Pant-y-daren Dolomite.

THIS STUDY	GEORGE ET AL. 1976	GEORGE 1954		CORAL-BRACHIOPOD ZONES (Robertson & George, 1929; Robertson, 1927; George, 1954.)	MAJOR CYCLES (Ramsbottom, 1973)	STAGE NAMES
LLANELLY FORMATION	LLANELLY FORMATION	CALCITE MUDSTONE GROUP		UPPER CANINIA ZONE (C_2S_1)	3	ARUNDIAN
GILWERN OOLITE	GILWERN OOLITE	OOLITE GROUP	GILWERN OOLITE	ZAPHRENTIS ZONE (ZC_1)		
CORAL BED+	CLYDACH BEDS		MARKER BEDS			
CLYDACH BEDS	BLAEN ONNEN OOLITE				2	CHADIAN
BLAEN ONNEU OOLITE			MIDDLE* OOLITE			
DAREN DDU BEDS					1	
PWLL-Y-CWM OOLITE	PWLL-Y-CWM OOLITE		PWLL-Y-CWM OOLITE			
UN-NAMED DOLOMITE						
LOWER LIMESTONE SHALE	LOWER LIMESTONE SHALE	LOWER LIMESTONE SHALE		CLEISTOPORA ZONE (K)		COURCEYAN

* Un-named by George. Name used by Owen et al, 1965.

+ Named by George, 1954

Fig.1/3 STRATIGRAPHY AND NOMENCLATURE

Diagram showing the stratigraphy and the development of the nomenclature of the lower portion of the Carboniferous Limestone in the study area.

1.2 Lithological description and environments of deposition

Lithological descriptions

The various rock units that make up the Oolite Group are described below. This information is summarised in Fig. 1/4.

Pwll-y-cwm Oolite

The Pwll-y-cwm Oolite forms a massive unit approximately 8 m. thick. In the east of the area it is completely dolomitised. Dolomitisation progressively decreases west of Cwm Dyar, although, as far west as Craig y Gaer, small areas are sporadically completely dolomitised. Further west than this, dolomitisation is virtually absent.

In the Clydach area the Pwll-y-cwm Oolite is dark with a pungent odour (H_2S?), although weathered surfaces are white. The base of the oolite is bioclastic, containing brachiopods, bivalves (as micrite envelopes, Bathurst (1966)), bryozoa, echinoderm and ostracod remains as well as ooids. The brachiopods vary in their state of preservation from intact, unbored shells to small, rounded, highly bored fragments of valves. There is much evidence of early diagenetic pyrite. This facies grades upwards into a pure, well sorted oosparite containing structureless 'algal balls', similar to allochems called rhodolites by Becker and Moore (1979), which are slightly larger than the ooids (Fig. 1/5). These and other larger allochems are concentrated in thin, approx. ½ cm. thick, laminae that lie sub-parallel to bedding.

As one moves westwards the Pwll-y-cwm Oolite loses its dark, pungent character and is a pale sparite. The trend from bio-clastic to more oolitic facies upwards is still maintained, although the upper portion of the oolite contains appreciable

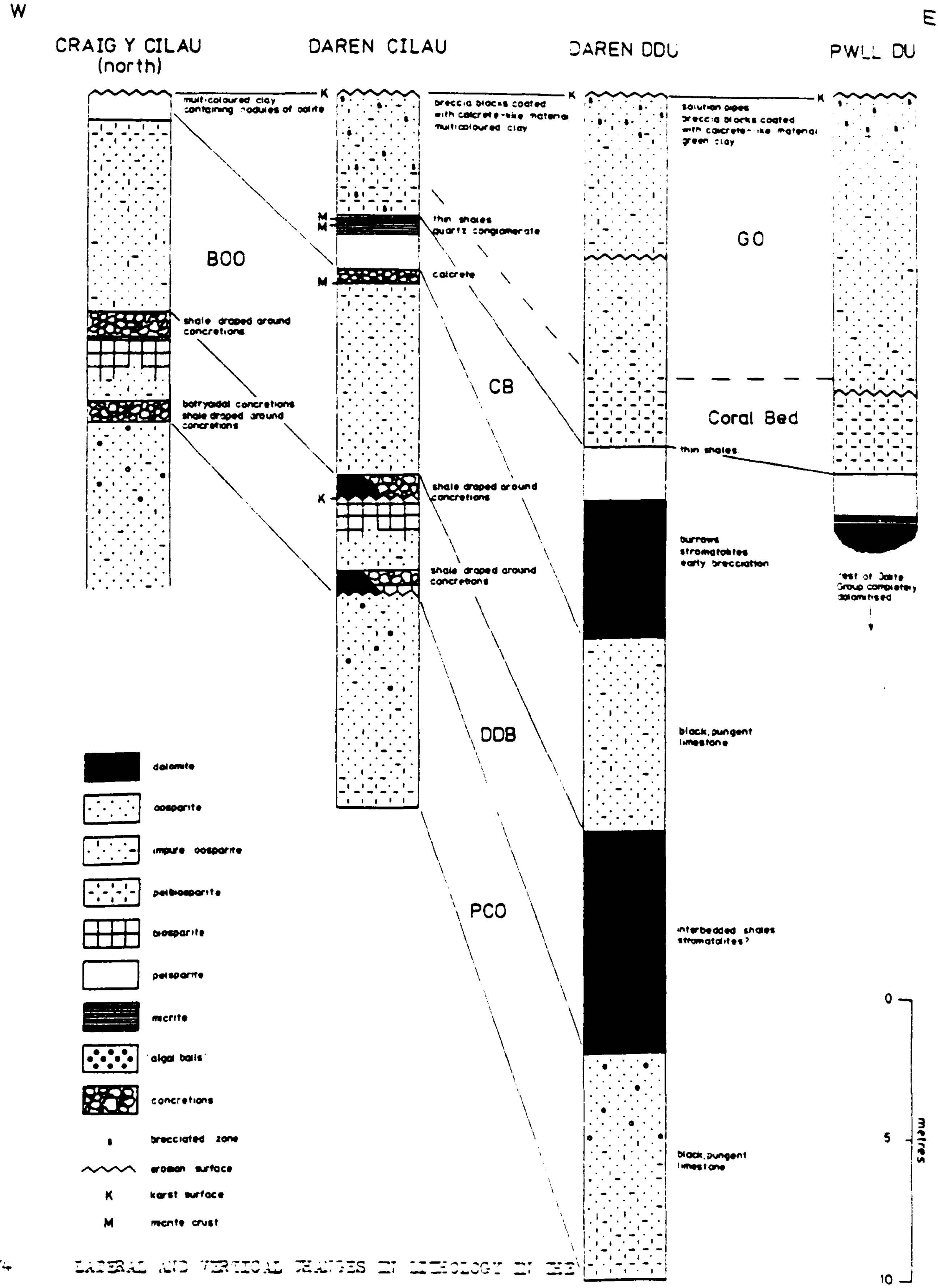


Fig.1/4 LATERAL AND VERTICAL CHANGES IN LITHOLOGY IN THE OOLITE GROUP

Four sections through the Oolite Group in the study area showing the lithologies encountered and their lateral and vertical variation. (GO - Gilwern Oolite; CB - Clydach Beds; BOO - Blaen Onneu Oolite; DDB - Daren Ddu Beds; PCO - Pwll-y-cwm Oolite)

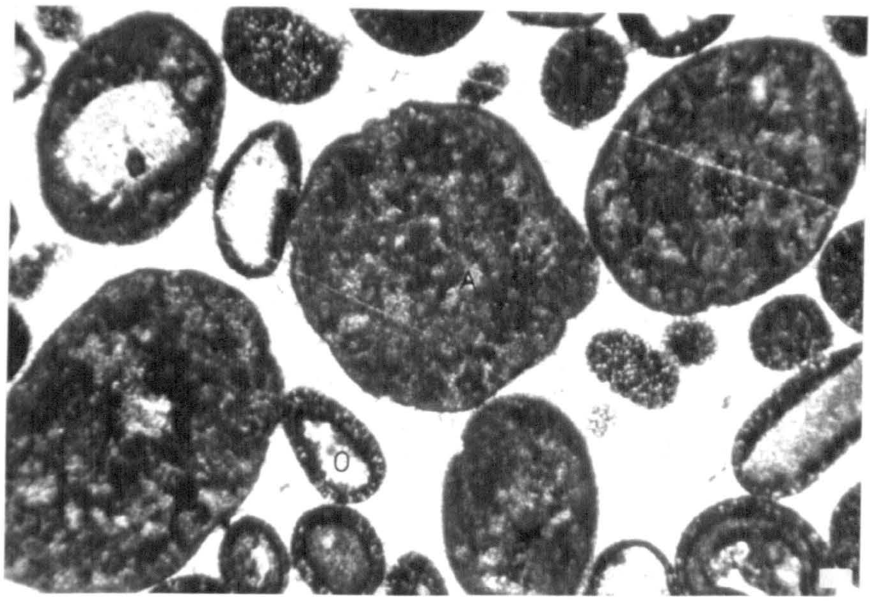


Fig.1/5 'ALGAL BALLS'

Transmitted light photomicrograph showing 'algal balls'(A) and ooids(O).
Sample 17843.

numbers of bioclastic grains, mainly from brachiopods and echinoderms as well as the 'algal balls'. Again these tend to be concentrated in laminae sub-parallel to bedding. Brachiopod valves are oriented convex surface upwards suggesting the action of moving water.

The top of the oolite is usually flat. At Chaw Pant-y-rhiw vertically walled pits, up to 4 cm. deep and 1 cm. wide, penetrate the top of the oolite and are filled with clay. These are possibly borings.

Sedimentary structures are generally not seen in the Pwll-y-cwm Oolite.

Daren Ddu Beds

The Daren Ddu Beds show a marked thinning and change in lithology westwards. From Coed Pant-y-daren eastwards they consist of fine grained dolomites and shales. These occasionally show poor algal laminations. Dolomitised biosparites can be recognised at Coed Pant-y-daren. West of this, dolomite is restricted to two beds, one at the top and the other at the bottom of the Daren Ddu Beds. The dolomite within these beds occurs either as bedded sheets which pinch out abruptly or as irregular to 'dune-shaped' units (Plate 1/1a, b). In the latter form, the steeper face always dips west. The dolomite is fine grained and usually structureless although occasionally signs of penecontemporaneous brecciation, algal laminations and burrowing are found. The dolomite alternates laterally with concretions which are described in Ch. 5 (Plate 1/1a) and, in the lower bed, with bioclastic rocks. The concretions are embedded in shale which drapes around them. The amounts of dolomite and bioclastic material decreases westwards being replaced by an increasing

a

b

Plate 1/1 THE QUARRY AT CHAW PANT-Y-RHIW

a)The Daren Ddu Beds, bounded by dolomitic/concretionary horizons, lie between the Blaen Onneu Oolite above and the Pwll-y-cwm Oolite below. Concretions can be seen alternating with dolomite lenses in the upper dolomitic layer. A concretionary layer, thought to be a calcrete, can be seen at the very top of the quarry. Total thickness of the sequence is 25m.

b)The surface below the upper dolomitic/concretionary horizon is undulating. Dolomite fills in the dips and hollows. Total thickness seen is 15m.

proportion of concretions. The shales, concretions and bioclastic sediments yield abundant conodont and vertebrate (scales, teeth, bone) remains. This partly explains a higher than average (4–7%) acid insoluble content. The lower biosparite contains authigenic glauconite.

The dolomitic beds are separated by 2½ m. of massive oobio- to biosparite. The proportion of ooids decreases upwards and they are absent from the top metre. The bioclastic fragments are dominantly of echinoderms, brachiopods and molluscs (bivalves and gastropods preserved as micrite envelopes), in the lower portion. In addition, bryozoa are present in the upper portion. The top of this unit has an undulating surface (Plate 1/1b), the hollows of which are filled in by the overlying dolomite.

Blaen Onneu Oolite

The Blaen Onneu Oolite is first identifiable at Daren Odu, east of which it is completely dolomitised. Like the Pwll-y-cwm Oolite of the Clydach area it is a massive, dark, pungent rock at Daren Odu. Elsewhere it is light in colour. It contains only 1–2% acid insoluble material. Its thickness is constant at approximately 9 m.

The oolite is mainly a poorly sorted, impure oosparite. Only very rarely is it a pure oosparite. Common bioclastic components include brachiopods, bivalves (as micrite envelopes), echinoderm plates and occasionally pellets. Larger bioclastic grains are usually concentrated in laminae sub-parallel to bedding, brachiopod and bivalve shells are oriented convex surface uppermost. In the top ½ m., ooids disappear and the rock contains much pellet and echinoderm debris.

Between Darren and Daren Cilau a 4½ cm. thick micrite crust is found on top of the oolite. This and the underlying marine sediments have a mottled green, brown and red colouration. This has been identified as a calcified soil profile (V.P. Wright, pers. comm.) This is overlain by a nodular horizon (Plate 1/1a) that is thought to represent a calcrete deposit. Burrowing, which predates nodule formation, is evident in some of the nodules. West of Daren Cilau the top of the Blaen Onneu Oolite is not exposed so it is not known whether these features continue westwards. They do not continue much further east than Darren. At Coed Pant-y-daren highly asymmetric dolomite 'pods' similar to those found in the dolomitic beds of the Daren Odu Beds further west, are found at the top of the oolite (Plate 1/2).

Clydach Beds

Like the Daren Odu Beds the Clydach Beds show a lateral thinning and change in lithology westwards. In the east they are predominantly dolomitised, only the top metre or so being unaffected. In the east, the dolomitised portion of the beds consists of fine grained dolomites and shales. The dolomites show algal and sedimentary lamination, burrowing and pene-contemporaneous brecciation. The undolomitised portion consists of shales, some up to 60 cm. thick, micrites, pelsparites and pelmicrites. Occasionally, oncolotic horizons occur. The shales become thinner and more infrequent westwards. Detrital quartz is common everywhere.

In the Darren to Daren Cilau area the base of the Clydach Beds consists of up to 2 m. of pelsparites and pelmicrites. Above this lies thin micrites, pelmicrites, intermittent coarse clastic beds (quartz grains having diameters up to 2 cm.) and

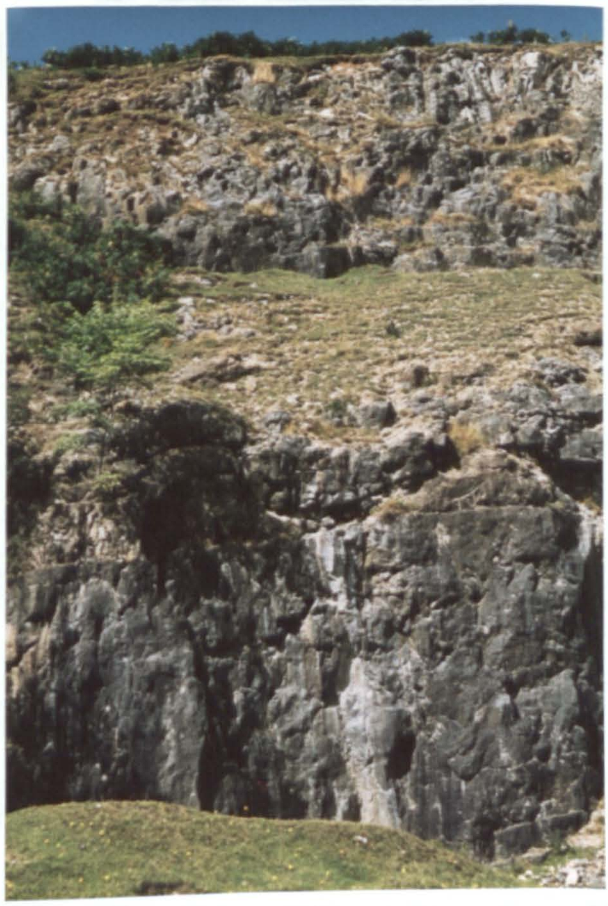


Plate 1/2 THE QUARRY AT COED PANT Y DAREN

The massive unit at the base is the Blaen Onneu Oolite.This is overlain by lenses of dolomite;the sides of these lenses can be very steep.The overlying bedding of the Clydach Beds (largely obscured by grass) drapes over the dolomite.The massive top unit is the Gilwern Oolite.Total thickness of the sequence is 30m.

thin micritic crusts; these are often stained red and green and may be associated with fibrous calcite layers which are similarly coloured (Plate 1/3). All the upper beds contain abundant detrital quartz. Most beds are separated by thin shales 1 - 2 cm. thick.

West of Daren Cilau the Clydach Beds are only, at best, poorly exposed. They thin and disappear westwards as a result of the erosion that occurred prior to Llanelly Formation sedimentation.

Gilwern Oolite

The Gilwern Oolite is a white, dominantly impure and poorly sorted oosparite. At most it contains only 1½% acid insoluble material. Unlike the other two oolites it does not have a black, pungent character in the Clydach area. It remains virtually unaffected by the dolomitisation that is pervasive in the underlying beds as far east as Pwll du, although locally it is completely dolomitised. In the east of the study area it reaches 14 m. in thickness. To the west, it thins and disappears as a result of erosion prior to Llanelly Formation sedimentation.

The base of the Gilwern Oolite is a coarse pelbiosparite: the Coral Bed of George (1954). The bioclastic components consist of brachiopods, bivalves and gastropods (as micrite envelopes) and echinoderm plates. Occasionally clasts of the underlying Clydach Beds are also present. Ooids are absent. The thickness varies from less than a metre to more than 2 m. At Twyn-y-dinas and Craig y Gaer the Coral Bed contains beds of pelsparite displaying parallel lamination and eroded upper surfaces. Angular clasts of pelsparite are included in the overlying limestone. In both these localities the Coral Bed

Plate 1/3 MICRITE CRUSTS

The upper surfaces of these samples, from the Clydach Beds at Chaw Pant-y-rhiw, are coated with micrite crusts. These are thought to have developed subaerially. Samples 20575 and 20576.

consists of 2-3 fining upwards cycles up to 50 cm. thick. Cross-lamination is commonly seen in the Coral Bed.

The Coral Bed grades upwards into an impure oosparite. As well as ooids, allochems include echinoderm plates, brachiopods and pellets; the latter occasionally being the dominant allochem. Occasionally intraclasts are also common. At Daren Odu an erosion surface is found within the oolite. The sediment immediately underlying this is a pure oosparite which grades downwards into the typical impure oosparite lithology. The ooids in the pure oosparite are distinct in that they are larger than those found in the impure oosparite and show an obvious radial-concentric structure, the ooids in the impure oosparite being completely micritised. In the Clydach area the top 1-2 m. of the Gilwern Oolite is also a pure, well sorted oosparite in which the ooids again are large with obvious radial-concentric structure.

Sedimentary structures are only rarely seen within the Gilwern Oolite, for instance at Twyn-y-dinas and Pwll du. Here they consist of cross laminated sets up to 20 cm. high.

The top 2 m. of the Gilwern Oolite is highly brecciated. The blocks in the breccia zone are surrounded by green clay. Solution pipes up to 1 m. long are found at Llanelly Quarry and Craig y Gaer. In these two localities a fissure zone exists at approx. 2 m. below the top of the oolite. Both these features have been described and illustrated by Wright (1980, 1981, 1982). He interprets the fissure zone as a water table cave. A calcrete horizon is occasionally found above the oolite, elsewhere calcrete-like material may be found coating blocks in the brecciated zone. As the Gilwern Oolite thins and disappears westwards the brecciation described above affects progressively lower stratigraphic levels and to the west of Chaw Pant-y-rhiw disrupts the Clydach Beds and the Blaen Onneu Oolite.

Environments of deposition

The intention behind this study of the Oolite Group was to unravel the diagenetic history rather than to interpret the environments of deposition. However, some environmental interpretation must be made as the early diagenesis of the sediments will depend on the environment in which they were deposited. No attempt has been made to fit the sediments of the Oolite Group into a regional sedimentological model. That is beyond the scope of this study and the limited two dimensional section of the Oolite Group seen in the study area makes this impossible in any case. The reader is referred to Wright (1981) for a discussion of models previously suggested for this area.

Wright (1981) suggests that the rocks of the Oolite Group represent three cycles of sedimentation. These are typified by the following sequence. At the base is a biosparite which represents a transgressive phase. This grades upwards into oosparites which are true marine sands. Regression results in the oosparites being overlain by peritidal deposits which are seen in the Clydach and Daren Ddu Beds. These consist of shales, micrites, pelsparites and pelmicrites, stromatolites and calcretes. These cycles have been correlated with cycles 1-3 of Ramsbottom (1973), in Fig. 1/3.

Investigation of the lithofacies of the Bahamas Banks has shown that active ooid shoals consist almost exclusively of ooids. The oolitic facies on the lagoonal side of the active ooid shoals contains only 60-70% ooids, the rest consisting of pellets and bioclastic allochems (Purdy, 1963). For this reason the bulk of the oolites seen in the study area are thought to have been deposited, not as active ooid shoals, but rather as lagoonal sands, the ooids being washed from active ooid shoals further south and east. This would explain the general lack of sedimentary structures and the high degree of micritisation. The convex-upwards orientation of shells indicates the influence of moving water during their deposition. This and the concentration of larger allochems in sub-horizontal laminae may be the result of reworking of the sand during storms. Pure, well sorted oolites are found within the Oolite Group. The larger, unmicritised ooids found in these suggest a more active, shallower environment or deposition where micritising algae were not so active. Within the Gilwern Oolite this type of grain is associated with erosion surfaces. The erosion surface found in the middle of the Gilwern Oolite at Daren Ddu (described in 2/1) is of limited extent and the pure oosparite may well be associated with shoaling that resulted in the formation of a small island. The erosion surface found at the top of the Gilwern Oolite is associated with widespread exposure. The pure oosparite at the top of the Gilwern Oolite contains keystone vugs. These have been used to indicate sedimentation in a beach environment (Dunham, 1970). Cements from these sediments have been interpreted as beachrock cements (described in 2/1).

The Clydach and Daren Ddu Beds are considered to be peritidal deposits. The lateral change in these beds is considered to reflect facies changes as one approaches the shoreline. There is increasing indications of subaerial exposure in these beds as one moves westwards, i.e. shorewards, in the form of calcretes (on top of the Blaen Onneu Oolite), karsts and micrite crusts. There is increasing evidence of clastic input also.

It is not clear how the Daren Odu Beds of the west of the study area fit into this model. They are dominantly bio sparites and lie landwards of typical peritidal deposits. Sedimentation in the concretionary horizons was certainly very slow as evidenced by the presence of authigenic glauconite. It is not clear whether the concretions are calcretes or are of a later, diagenetic origin. Also the origin of the dolomite lenses is uncertain. The borrowing and brecciation suggests shallow to emergent conditions.

The breccia zone at the top of the Gilwern Oolite has been interpreted by Wright (1980, 1981, 1982) as a karst. He interprets the fissure at the base of the brecciated zone as a water table fissure, hence marking the paleowater table. The karst probably took several thousand years to form (Wright, 1980, 1981). The overlying calcrete is also a subaerial deposit and the change from karst to calcrete formation represents a major climatic change (Wright, 1980), from wet to arid conditions.

CHAPTER TWO

CEMENTATION

The cements of the Oolite Group were studied using a number of techniques. Thin sections were stained (Dickson, 1965) and examined with transmitted light. Selected thin sections were polished and their cathodoluminescence (CL) studied. Many thin sections were polished several times so it was necessary to start examination with a thick (40–60 μm.) section which made detailed study of fabrics difficult. Consequently, ultra-thin sections were made (approx. 10 μm. thick) for detailed fabric analysis.

The cements of the Oolite Group have been divided into two groups:-

1. 'Early' cements - those cements precipitated before or during the period of exposure which affected the top of the Oolite Group. This group will include the cements that formed contemporanously with sedimentation in the older Oolite Group units.
2. 'Late' cements - those cements precipitated after the exposure of the top of the Oolite Group.

2.1 'Early' cementation

Evidence which indicates that cementation was synchronous with deposition may be regarded as criteria for identifying 'early' cements and is outlined below:-

1. distinctive fabrics. Certain cement fabrics (fibrous, meniscus and cryptocrystalline cements for instance) develop in near surface diagenetic environments at the present day. Ancient examples of these fabrics presumably formed in similar environments. Although these recent cements are not always contemporaneous with deposition, this is usually the case. In the Oolite Group they are invariably the first cements precipitated.

2. the presence of diagenetic sediment (Dunham, 1969). The presence of diagenetic sediment has been used as an indicator of early cementation (Dunham, 1969; Meyers, 1978). The use of this criterion depends on the depth to which diagenetic sediment can penetrate. This is a function of the source of the fluids carrying the sediment and the environment in which it is introduced. Examination of thin sections makes it obvious that there was a major influx of diagenetic sediment between calcite and later ferroan calcite cementation. The introduction of this sediment can be dated as after exposure and hence this criterion must only be used in conjunction with other evidence.

3. cements cut by intraformational erosion surfaces. Cements cut by erosion surfaces must pre-date the erosion event.

4. cements present only below erosion surfaces. These cements mark a cementation event that preceded the deposition of the overlying sediments.

5. intraclasts (Folk, 1959). The origin of most limeclasts (Wolf, 1963) is unknown. They may either be intraclasts or extraclasts (Wolf, 1965). Care must be taken to identify

true intraclasts if they are to be used as indicators of 'early' cementation. Intraclasts can be used in the same way as intraformational erosion surfaces in identifying 'early' cements.

6. cements overlain by deposits known to be associated with the exposure of the top of the Oolite Group. This feature is associated with calcrete-like cements and clay.

7. by correlation with known 'early' cements. Correlation on the basis of characteristic fabric and zonation, as revealed by staining and CL, with similar features in cements that are known to be 'early' can be used to identify 'early' cements for which there is no other evidence.

The bulk of the 'early' cements that are found are associated with the exposure surface at the top of the Gilwern Oolite. Therefore these are considered first. The 'early' cements from the rest of the Oolite are then catalogued.

<u>'Early' cements associated only with the top of the Gilwern Oolite</u>

The subaerial exposure surface at the top of the Gilwern Oolite has been described in Chapter 1. The solution piping and brecciation that occurs at this surface could only have developed in an indurated sediment, indicating that 'early' cementation occurred at this level. There is a clear sequence of cements developed at the top of the Gilwern Oolite, although some of these are very restricted in their occurrence. They are summarised in Fig. 2/1 and are described in detail below, starting with the oldest.

CEMENT TYPE	ENVIROMENT	POSITION RELATIVE TO WATER TABLE
calcrete	meteoric	vadose
meniscus	meteoric	vadose
	EROSION/KARSTIFICATION	
sparry	meteoric	phreatic
fibrous	marine ?	phreatic
cryptocrystalline	beach?	vadose

TIME

Fig.2/1 THE DEVELOPMENT OF 'EARLY' CEMENTS AT THE TOP OF THE GILWERN OOLITE

Table showing the sequence of 'early' cements developed at the top of the Gilwern Oolite and the environments in which they were precipitated.

Cryptocrystalline cements:

When found these cements are the earliest present. They are rare and in only one sample are they abundant. They are restricted to the top metre of the Gilwern Oolite and none have been found west of Craig y Gaer.

The cement is dark brown in colour and very finely crystalline (approx. 2 μm). The lack of coarse detritus within the calcite suggests that it is not an internal sediment. The outer edges of the cement are concave and it shows an increased thickness at the bottom of pores (Fig. 2/2a,b), on some occasions producing a flat base. It may be absent from the top of pores, other pores are completely filled.

The CL of this cement is dull, similar to the allochems (Fig. 2/2b). The grain size is too small to detect any possible variation in CL intensity within individual crystals.

The concave outer margins of the cement are reminiscent of meniscus cements (Dunham, 1971), which would indicate vadose precipitation. The thickening of the cement at the bottom of pores and the flat base that this sometimes produces could be the result either of precipitation of the cement from pools of water sitting at the bottom of pores or the settling out of fine grained sediment from suspension. The former would occur in the vadose environment, the latter could occur in the phreatic environment. As mentioned previously an origin as internal sediment is thought unlikely, although Taylor & Illing (1969) do describe internal sediment forming 'pronounced collars' at grain contacts.

Cryptocrystalline cements have been found forming in marine related environments, both below and above sea-level (Shinn, 1969; Taylor & Illing, 1969). Fine grained 'calcrete' cements will be

Fig.2/2 'EARLY' CEMENTS FROM THE TOP OF THE GILWERN OOLITE

a)Transmitted light photomicrograph of cryptocrystalline cements showing strongly curved margins and thickening at the base of pores (A).This cement is virtually absent from the top of pores (B).Sample 18338.

b)Cryptocrystalline cements forming menisci.Sample 17865.

c)Transmitted light photomicrograph showing asymmetrical 'fibrous' cements (F) Crude concentric banding can be seen within the 'fibrous' rim.Sparry calcite (S) occurs within part of the 'fibrous' rim.Sample 21657.

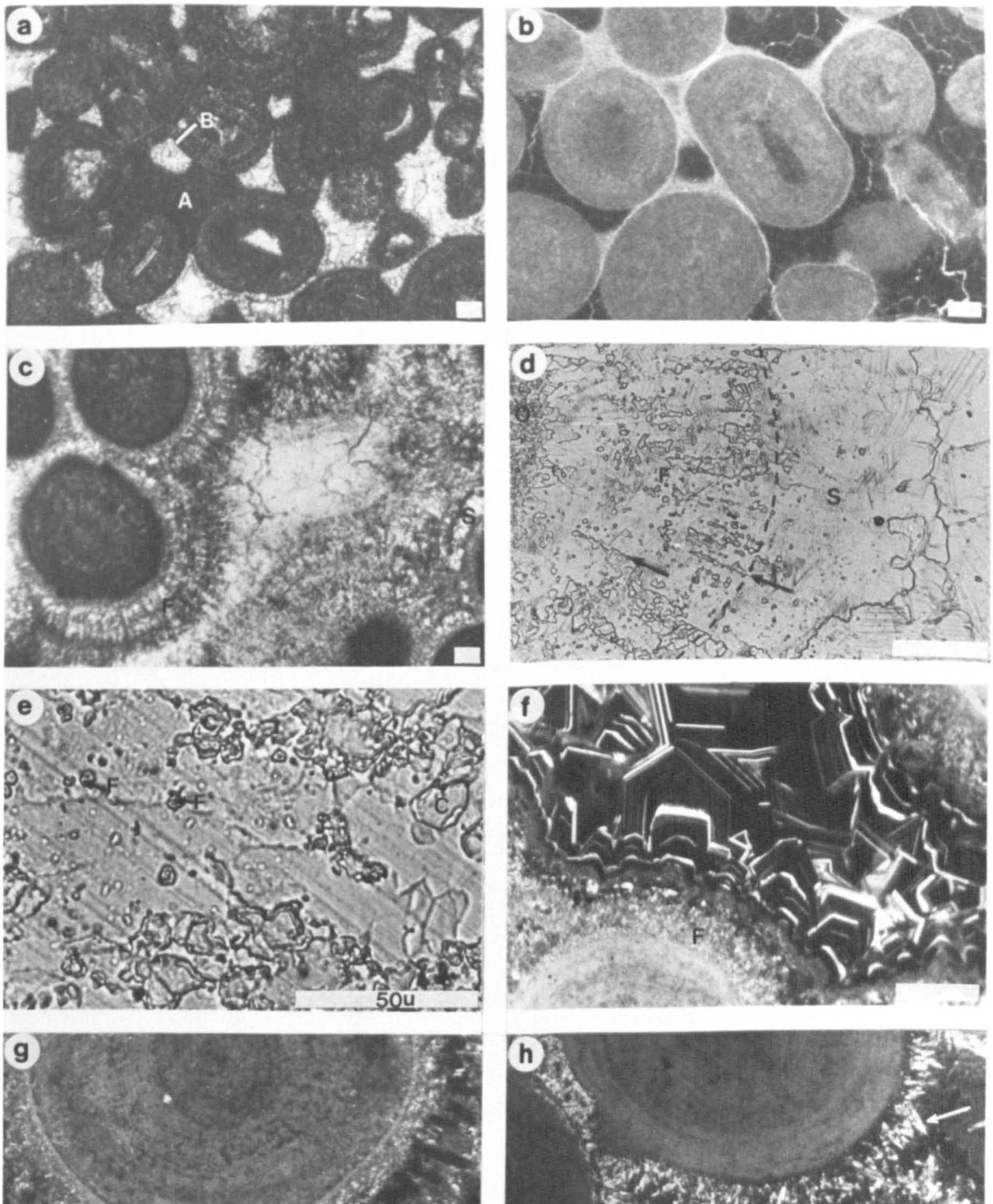
d)Transmitted light photomicrograph of an ultra-thin section.'Fibrous' cement (F) contains carbonate inclusions concentrated along its crystal boundaries (arrows).The junction between the 'fibrous' cement and the overlying sparry calcite (S) is marked by a dashed line.The sparry calcite grew syntaxially on the 'fibrous' calcite but contain no inclusions along their boundaries. Sample 21657.

e)Transmitted light photomicrograph of an ultra-thin section.Close-up of the 'fibrous' rim showing fluid inclusions with vapour bubbles (F) and carbonate inclusions (C).Sample 21657.

f)The 'fibrous' rim (F) has an irregular luminescence containing brightly luminescing spots.Sample 21657.

g)Elongate,non-luminescing areas which radiate from the ooid substrate are seen in some 'fibrous' rims (F).These are interpreted as the original crystal fabric.Sample 21657.

h)Patchy,brightly luminescing 'fibrous' rims around ooids.On occassion the luminescence picks out needle-like shapes (arrow).Sample 21657.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described later which, in transmitted light, are indistinguishable from these, although a distinction can be made using CL. Thus it seems unlikely that these are calcrete-like cements. The meniscus distribution and the thickening at the base of pores probably reflects precipitation above the water table and the cryptocrystalline habit suggests a marine dominated environment of precipitation. Precipitation in a beach or intertidal setting would seem appropriate especially as they are found in sediments containing keystone vugs (discussed in 1/2).

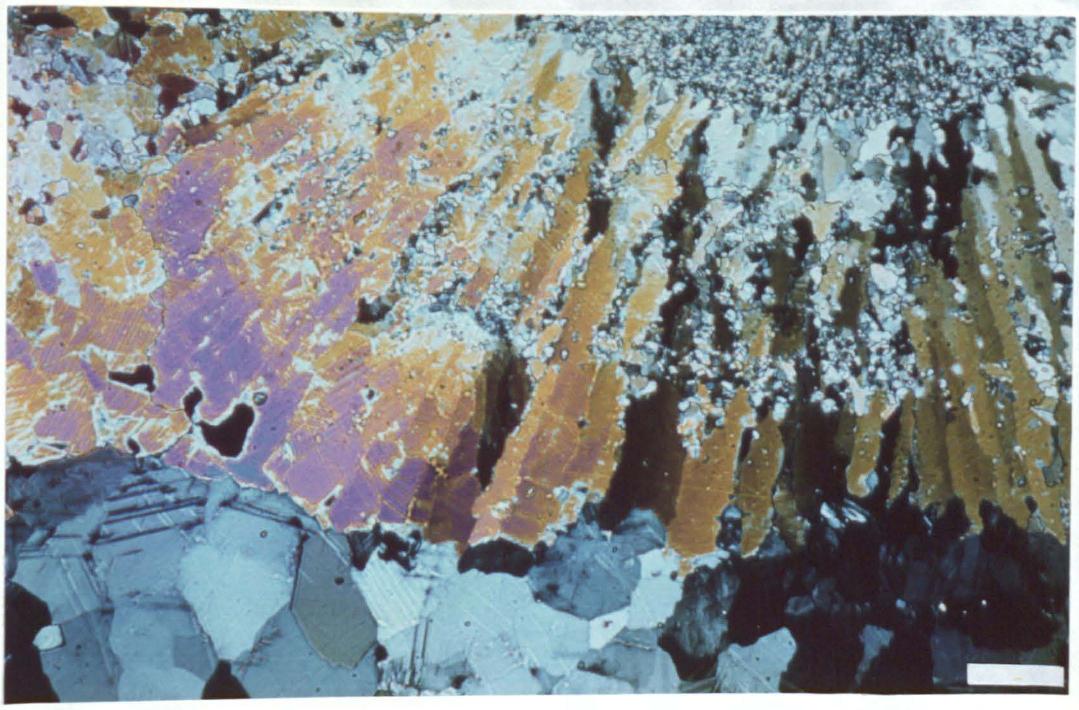
'Fibrous' cements

Only one unusual occurrence of fibrous cement has been found. The single example comes from the very top of the Gilwern Oolite at Llanelly Quarry. There is a thick development of what is presumed to have been fibrous carbonate lining near vertical, elongated vugs in the oolite. These are approx. 5 mm.wide, at least 1 cm. high and of unknown lateral extent. The growth around ooids is highly asymmetrical, occurring preferentially into the vugs, being up to four times thicker into, rather than away from, the vugs (Fig. 2/2c). The maximum development is approx. 5 mm. thick normal to the substrate. Fibrous growth on ooids not immediately adjacent to the vugs is thin or absent. Crude concentric banding is the result of variations in inclusion density. Occasionally concentric bands of sparry calcite are present within the 'fibrous' rim (Fig. 2/2c) and elsewhere sparry calcite may lie between ooid and the 'fibrous'rim where the latter has spalled away from the ooid.

Examination of ultra-thin sections reveals that the 'fibrous' cement rim is composed of elongate crystals that taper towards the ooids and that lie perpendicular to the ooid surface (average dimensions: width 10–15 μm, length 300 μm). Individual crystals rarely extend the entire width of the rim; this may be due to the plane of the section not lying parallel to the elongation of the crystals. Twinning is common and occasionally twin planes are curved (concave towards the substrate). Under crossed polars the crystals show progressive extinction as the stage is rotated (Plate 2/1a). Individual crystals may show undulose extinction. The contacts between the elongate crystals are irregular and equant carbonate inclusions with sutured contacts clustered along them (Fig. 2/2d). The inclusions vary in size and shape, but are approx. 5–10 μm. across. Similar carbonate inclusions are found within the elongate crystals, as well as small fluid inclusions with vapour bubbles (1–2 μm), but they are not common (Fig. 2/2e). Under crossed polars the carbonate inclusions do not extinguish in continuity with the elongate crystals (Plate 2/1b). The sparry crystals outside the 'fibrous' rim have grown syntaxially on the elongate crystals (Plate 2/1a). No carbonate crystals are found within or along the contacts of these crystals, also the contacts are straighter than the contacts between elongate crystals in the 'fibrous' rim. There is no evidence of a former acicular precursor, e.g. needle-like inclusions (Kendal & Broughton, 1978) within the elongate crystals.

The CL of the cement is very irregular. It is generally dull, but is dotted with brightly luminescing patches (Fig. 2/2f,g). Occasionally it is dominated by very brightly luminescing calcite (Fig. 2/2h). Rarely elongate, parallel sided, non-luminescing areas are seen radiating from the substrate (Fig. 2/2g). These areas do not typically extend the full width of the rim nor do they necessarily originate from the ooid substrate. The form of

a



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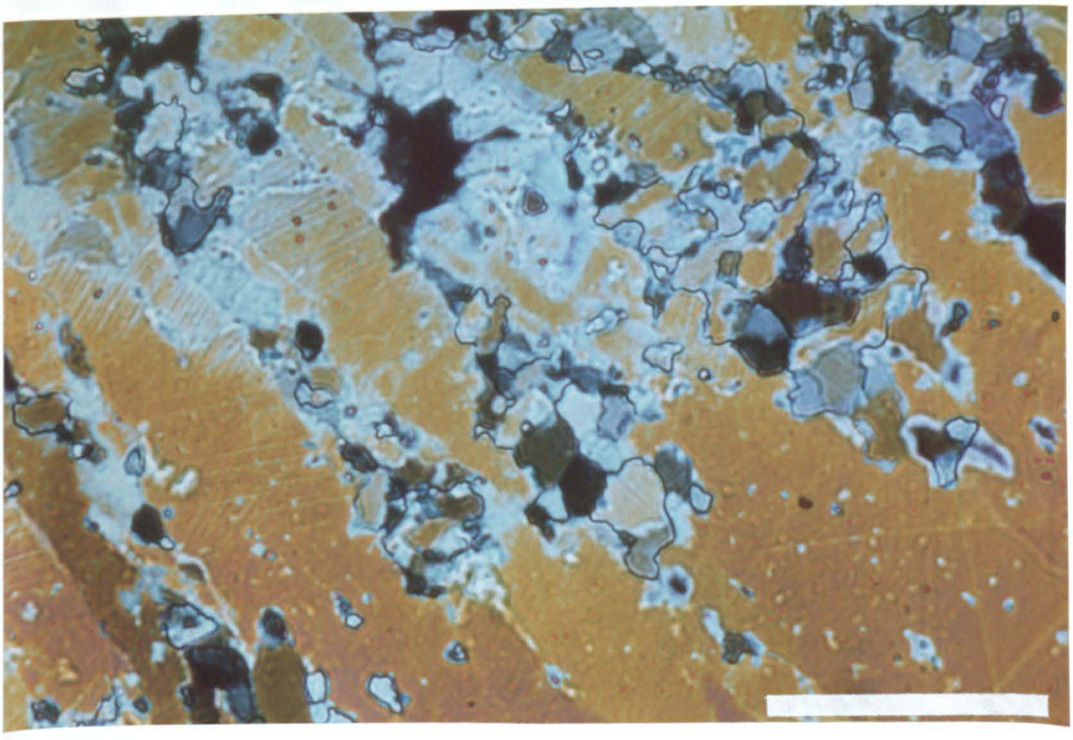


Plate 2/1 'FIBROUS' CALCITE

a) Transmitted light photomicrograph of an ultra-thin section of 'fibrous' calcite viewed under crossed polars. The outer limit of the inclusions marks the edge of the 'fibrous' calcite. Later calcite grew syntaxially on the 'fibrous' crystals. The 'fibrous' crystals show sweeping extinction.

b) Transmitted light photomicrograph of an ultra-thin section of 'fibrous' calcite viewed under crossed polars. Carbonate inclusions are concentrated between the crystals. They do not have a similar optical orientation as the 'fibrous' crystals.

the terminations of these areas are often diffuse and hard to define. In Fig. 2/2g they appear square-ended, elsewhere they have sharp terminations (Fig. 2/2h). The dimensions of the individual non-luminescent areas are of the same order or magnitude as the elongate crystals identified in transmitted light, the only difference being that the crystals seen in transmitted light are tapered whereas the dark areas seen with CL are not.

Since the original cement crystals were parallel sided, there must initially have been gaps between these crystals which no longer exist. If they were filled by the syntaxial growth of carbonate on the cement this would explain the difference in shape between the original cement crystals and those now seen in transmitted light (Fig. 2/3 1 and 2). Therefore the rims are the combination of original cement and later filling material. The irregular boundaries between the crystals may reflect the uneven filling of the primary porosity within the original cement and/or the effects of later diagenetic processes. The occurrence of carbonate inclusions with random orientation can be explained either in terms of a solution model, summarised in Fig. 2/3, or as the result of recrystallisation. The distribution of inclusions dominantly along crystal boundaries is similar to that found by V.P. Wright (1982) for fibrous crystals from the Llanelly Fm. He attributes these to the process of degrading recrystallisation. Similar recrystallisation features are described by Borak & Friedman (1981). If the carbonate inclusions are the result of this process, it must have occurred prior to the precipitation of the overlying sparry cements, since these do not contain inclusions along their crystal boundaries, i.e.

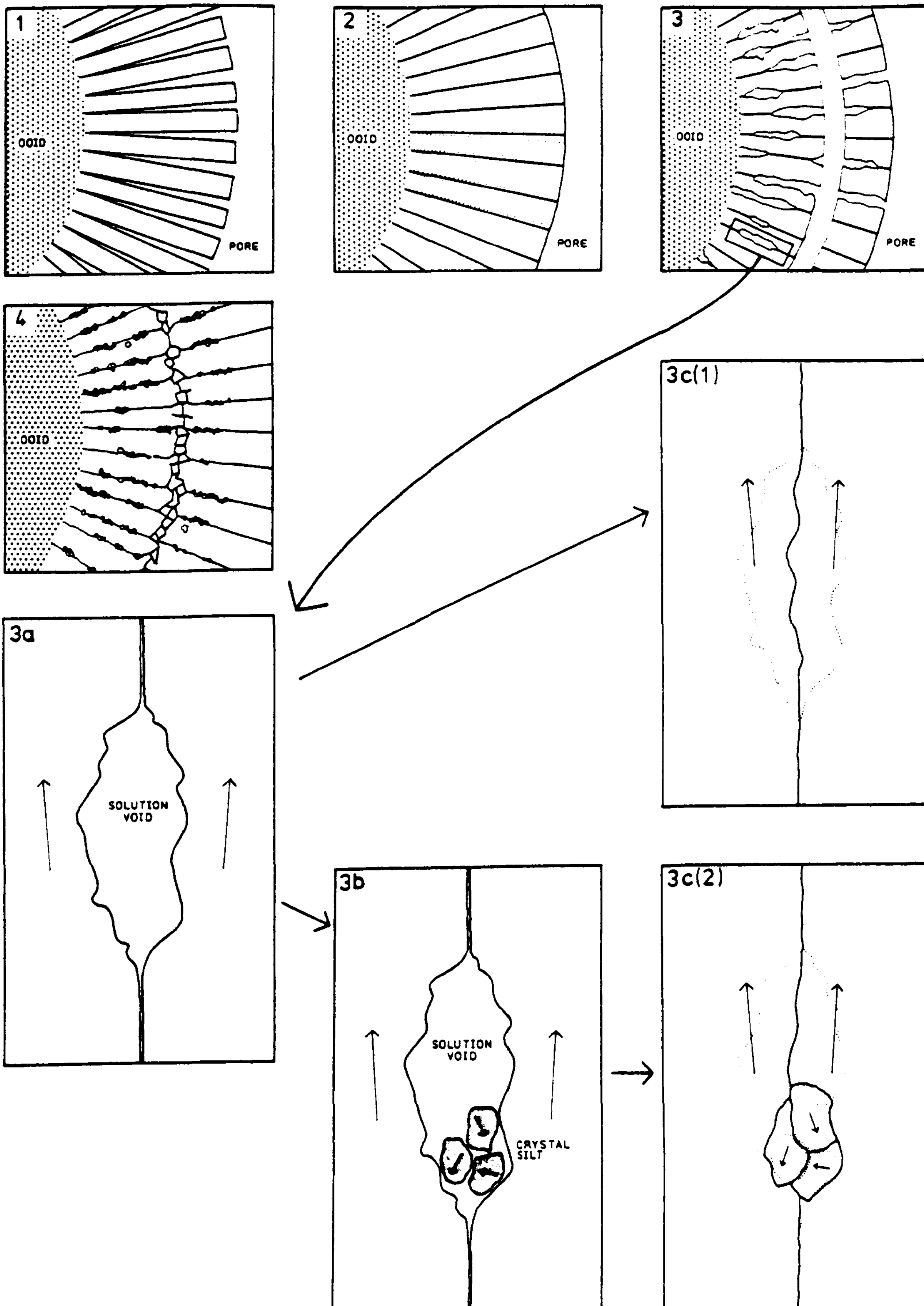
Fig.2/3 THE DEVELOPMENT OF 'FIBROUS' CEMENT FABRIC

1) Parallel sided fibrous cement crystals grow on ooids.

2) The space between the fibres is filled by later cement. The dotted lines mark the position of former cement crystals.

3) Solution occurs. This can result in the removal of entire bands of the rim. Solution can also occur along crystal boundaries producing solution voids (3a). The arrows indicate the c-axis extinction position. Crystal silt (either fine grained carbonate sediment that is washed in or pieces of the cement rim itself detached by solution) accumulate in the solution void (3c). The crystallographic orientation of the crystal silt differs from that of the host crystals. Filling of the void by the syntaxial growth of carbonate yields an irregular junction with carbonate inclusions along it; the crystallographic orientation of the inclusions being unrelated to that of the host crystal (3c(2)). Where no crystal silt is introduced syntaxial filling results only in an irregular junction. (3c(1)). The edge of the former void is marked by a line of dots.

4) The later precipitation of sparry calcite, which grows syntaxially on the rim, is the final stage in the development of the fabric and completely fills all pore space.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3c(1)
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SOLUTION
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SOLUTION
VOID
CRYSTAL
SILT
3c(2)

recrystallisation was an 'early' phenomenon. However, it seems probable that raised temperatures, although below metamorphic conditions, are necessary for degrading recrystallisation to occur. Also, the few examples of degrading recrystallisation that do exist are restricted to crystals much larger than those described here (Voll, 1960; Wardlaw, 1962; Tucker & Kendall, 1973; Borak & Friedman, 1981).

The presence of bands of sparry calcite within the rims and the patchy nature of the CL is most likely due to dissolution processes. This lends more credibility to the solution model for the origin of the carbonate inclusions. In the former case, bands have been selectively removed from the rims and filled with later sparry calcite. The latter characteristic reflects smaller scale, more pervasive solution, the resulting voids being filled by brightly luminescing calcite. Brightly luminescing calcite filling solution vugs in inclusion-rich syntaxial overgrowth are described in 3.2. The gross morphology of the crystals as seen in transmitted light, is basically unchanged by this small scale solution process since voids are filled by the syntaxial growth of calcite on the etched crystal surfaces. Solution must have occurred after filling of the primary porosity of the rim, but prior to the precipitation of the sparry calcite since patchy brightly luminescing calcite occurs throughout the entire rim but is absent from the overlying sparry calcite. In most cases this process has completely obliterated the original CL fabric, hence the rare occurrence of the original cement crystals. Unfortunately, the crystal size is too small to check the distribution of the brightly luminescing calcite to see if it agrees with that predicted by the model outlined in Fig. 2/3.

Although some crystals display a slightly radiaxial fibrous habit, the luminescence is very different to that described for radiaxial fibrous calcite crystals by Lohmann & Meyers (1977). This, together with the lack of evidence of an acicular precursor and the preservation of apparent relics of the original cement crystals, suggests that the rim is not the result of recrystallisation of an acicular precursor (Kendal & Tucker, 1973). Undulose extinction is by no means common and could be attributed to the application of late tectonic stress (a common feature throughout the Oolite Group, see 2.5).

The original cement crystals seen using CL are similar to modern aragonite, marine cements described by Shinn (1969), Milliman (1974), Bathurst (1975) and others. This would suggest that they were originally marine precipitates. However, the asymmetry of the rims is unusual. The preferred direction of growth is governed only by the orientation of the vug and is irrespective of any 'way-up' effects, so a phreatic environment seems most likely. Presumably the vugs contained a micro-environment that was more suitable for cement precipitation than elsewhere in the sediment, the rapid fall off in thickness of the cement away from the vugs reflecting a chemical gradient between the vugs and the surrounding pores. The origin and nature of the microenvironment within the vugs is a mystery. An original aragonite minerallogy would explain the extensive 'early' solution which these crystals have undergone.

Sparry Calcite

Sparry cements occur both as drusy rims and completely filling pores. Drusy rims are up to 50 µm. wide (Fig. 2/4a,5a). There is no thickening of the rim at pore throats. The cement is

Fig.2/4 'EARLY' CEMENTS FROM THE TOP OF THE GILWERN OOLITE

a)Transmitted light photomicrograph showing a drusy cement rim (A) developed on ooids (O) and overlain by a cutan (C) and ferroan calcite (Fe).Sample 18338.

b)The same area as shown in (a).The drusy rim (A) is non-luminescing.Sample 18338.

c)'Early' phreatic cement developed on an ooid (O).An unconformity in the sequence (arrow)is overlain by brightly luminescing calcite.Sample 18322.

d)Syntaxial overgrowth on echinoderm fragment (E).The same CL zones are developed on ooids (O),but are thinner.NB:the CL zonation is very similar to that seen in (c) despite coming from a different location.Sample 18316.

e)'Early' phreatic cements developed on ooids.Sample 17843.

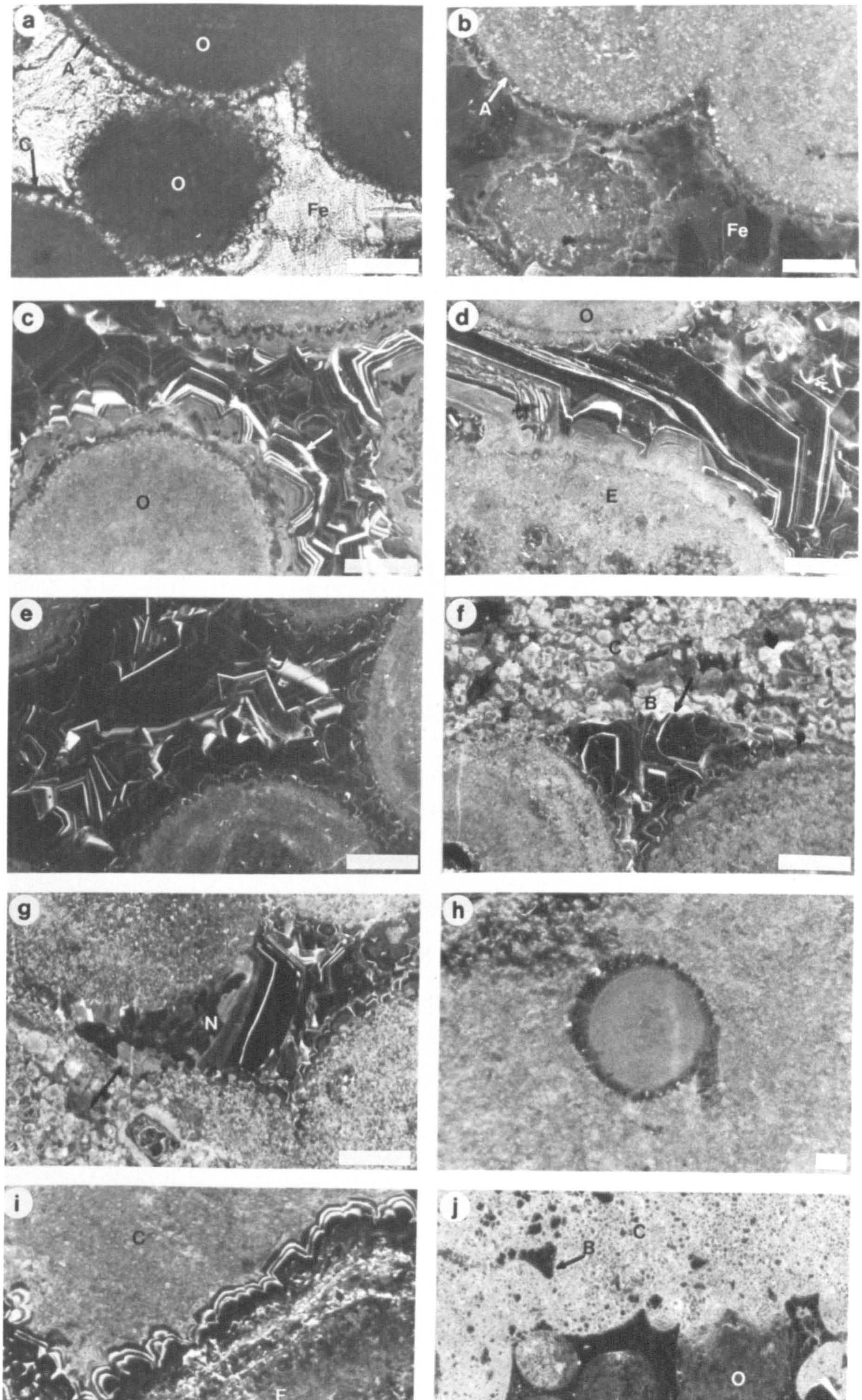
f)'Early' phreatic cements cut by an erosion surface and overlain by calcrete (C).Brightly luminescing sparry calcite (B) is growing on top of truncated spar (arrow).Sample 17843.

g)'Early' phreatic cement cut by an erosion surface.The dull luminescing zone is clearly truncated (arrow).This zone contains an irregular area of non-luminescing calcite (N).Sample 17843.

h)Calcrete containing an ooid that has retained its cement rim.Sample 21662.

i)'Early' phreatic cement overlain by calcrete (C).The sparry cement is growing on top of fibrous calcite (F).Sample 21665.

j)The junction between oolite (O) and calcrete (C).The calcrete clearly overlies non-luminescing sparry calcite.The scalloped margin of the cement indicates the former position of allochems.'Shards' of cement (S) are contained within the calcrete.Sample 18354.



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non-luminescing (Fig. 2/4b). In many cases it is overlain by what is presumed to be a clay film which was probably introduced during exposure. These are interpreted as cutans (Brewer, 1964; Meyers, 1978). The cement rim is easily distinguishable when it is covered by a cutan or when it is directly overlain by ferroan calcite (Fig. 2/4a), but it is harder to see when overlain by non-ferroan calcite. This type of cement has been identified along the length of the Gilwern Oolite where studied. It extends from the upper surface of the oolite as far as the fissure zone (2 m.) in the Clydach area and approx. 1 m. elsewhere.

Above the fissure zone, pore space is largely filled by 'early' sparry calcite, as are cobbles of the Gilwern Oolite found within the overlying Llanelly Fm. (Wright, 1981, 1982). This is in marked contrast to below the fissure zone where appreciable amounts of 'late' non-ferroan and ferroan calcite are present. In the fissure zone itself there is little cement, the only large crystals being syntaxial overgrowths on echinoderm fragments. Here most of the pores are filled with clay and there is much pressure solution between the ooids and between ooids and syntaxial overgrowths. Ooids encapsulated in syntaxial overgrowths are not affected by pressure solution. Pore filling sparry calcite cements are illustrated in Figs. 2/4c-j. That they are pre-exposure in age is proved by the application of the criteria outlined previously (Fig.2/4f-j). The largest, most complete and most easily studied cement sequences occur in syntaxial overgrowths on echinoderm fragments (Fig. 2/4d), but equivalent cements are also seen around ooids (Fig. 2/4c).

The initial overgrowth is usually composed of inclusion-rich calcite, but the density of the inclusions is very variable and they maybe almost absent. This is followed by inclusion-free calcite. A thin, faintly ferroan zone is occasionally found separating the two. CL reveals a lot more detail. Each of the three zones described above has a distinctive luminescent character:

1. inclusion-rich calcite. This is dominantly non-luminescing but often contains irregular patches of dull and brightly luminescing calcite;
2. ferroan calcite, where present, is represented by a dull luminescing zone. This luminescing zone is also present in samples where no ferroan calcite was evident. This may reflect the insensitivity of the staining technique to very small amounts of iron, or could be a true representation of the situation. This zone sometimes contains irregular, non-luminescing patches that cut across the zonation (Fig. 2/4g). These are discussed in 3.2.
3. clear calcite. This is dominantly non-luminescing but contains a brightly luminescing, hairline zonation pattern.

The clear, sparry calcites show no evidence of characteristic vadose fabrics. Their 'early' formation, clear sparry nature and zonal geometry (Meyers, 1974) suggests a phreatic meteoric origin. The origin of the initial inclusion-rich calcites and their patchy luminescence will be considered later.

Meniscus cements

Meniscus cements are best seen in the fissure zone as here there is little other calcite cement. They are never found in the rocks overlying the fissure zone in which the pores are filled by sparry calcite. For this reason they are thought to post-date the pore filling calcite. They are usually intimately associated with the cutans previously mentioned (Fig. 2/5a, b). The cutans are often continuous with the cements that bridge across the pore throats. The amount of clay within these cements makes them dark.

At Daren Cilau the menisci are formed by clear, non-luminescing calcite (Fig. 2/5c). These do not show the typical smooth, concave surfaces of menisci (Halley & Harris, 1979), but are spikey. This is due to overgrowth of later calcite. When non-luminescing calcite completely fills the pores the menisci are almost totally obscured, even using CL (Fig. 2/5d). As with the other 'early' cements, meniscus cements are patchily developed. Most samples from the top of the Gilwern Oolite show no recognisable meniscus cements.

As Dunham (1971) pointed out, meniscus cements invariably result from precipitation in the vadose environment. It is unusual to find much clay within them, presumably this reflects the large amount of clay associated with the exposure surface. Green clay is found within the breccia zone at the top of the Gilwern Oolite. The lack of meniscus cements below the fissure zone is consistent with this marking the water table (see 1.2).

'Calcrete' cements

Microspar is found filling the pores of some samples from the top metre of the Gilwern Oolite. It post-dates some sparry calcite (Fig. 2/5 e-g). CL reveals that it is made up of zoned rhombs, identical to those found in the overlying calcrete (Fig. 2/5h). Therefore, it is considered to have formed in a similar way and at the same time as the calcrete. In one sample micro-spar of two differing grain sizes was found (Fig. 2/5g). Exact equivalents of these two microspars can be found in the overlying

Fig.2/5 'EARLY' CEMENTS FROM THE TOP OF THE GILWERN OOLITE

a)Transmitted light photomicrograph showing ooids with a drusy cement rim overlain by cutans (C) that form menisci (M) at pore throats.Sample 22361.

b)Transmitted light photomicrograph showing cutans lying directly on ooids and forming menisci (arrow) at pore throats.Sample 22361.

c)Non-luminescing,sparry meniscus cements (arrows) are overlain by brightly luminescing cement.Sample 18354.

d)Meniscus cements (arrows) are almost totally obscured by later,dominantly non-luminescing,calcite.Sample 18354.

e)Transmitted light photomicrograph showing a syntaxial overgrowth (S) on an echinoderm fragment overlain by microspar (C).Sample 17858.

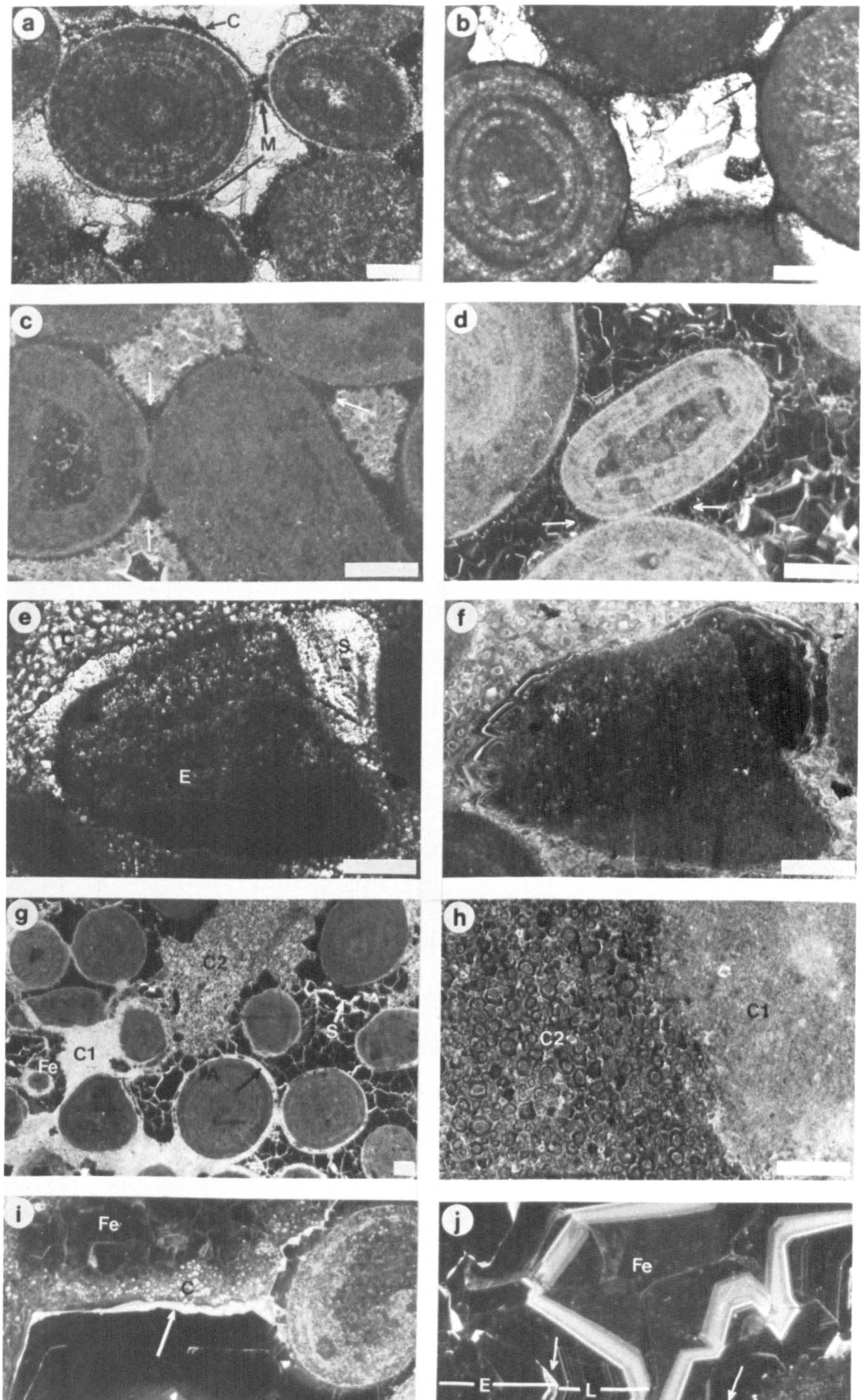
f)The same area as shown in (e).The microspar consists of zoned rhombs.Sample 17858.

g)Two types of microspar fills pores.The earlier (C1) is finer grained and has a more even CL than the later one (C2),which can be seen to be made of zoned rhombs.C1 lies between ooids and cement in spaces produced by the spalling of the cement from the ooids (arrow).A fractured ooid is also filled with C1.Crystal boundaries have been pulled apart and are now lined with brightly luminescing calcite (S).C2 is restricted to primary porosity. Remaining pore space is filled with ferroan calcite (Fe).Authigenic feldspar can be seen (A).Sample 17865.

h)Calcrete showing two different components,C1 and C2.Note the similarity of these to the microspar illustrated in (e) - (g).Sample 18310.

i)A veneer of brightly luminescing calcite coats a cement crystal (arrow). Microspar (C) rests geopetally upon it.The outer surface of the non-luminescing calcite is irregular,perhaps the result of etching.The final porosity is filled by ferroan calcite (Fe).Sample 20537.

j)'Early' and 'late' cements (E and L) filling a pore.The outer edge of the 'early' calcite has a veneer of brightly luminescing calcite (arrow).The final pore space is filled by ferroan calcite (Fe).Sample 22361.



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calcrete (Fig. 2/5h). The earlier of the two is finer grained and brightly luminescing, the later one is coarser grained and CL reveals zoned rhombs. The earlier one lies between cement that has spalled from its original ooid substrate and that ooid. This requires the cement framework to have expanded. This has resulted in crystal boundaries pulling apart and the spaces thus produced have been filled with brightly luminescing calcite. The later microspar only occurs in large primary pores that were never completely filled with sparry calcite. The restriction of the earlier microspar to pores produced by spalling and the later microspar to primary porosity is not understood. Nor is the process causing expansion. However, this is not the only example of expansion fabrics associated with 'calcrete' cements.

Sparry calcite associated with calcrete formation

A thin, often irregular, brightly luminescing calcite layer is sometimes found on crystals cut by the karst surface and on crystals within the oolite itself (Fig. 2/4f, 5i, j). Where present within the oolite the surface that it coats is often irregular (Fig. 2/5i) and does not represent the original crystal face. The uneveness of the surface is probably the result of etching. This cement is interpreted as being associated with the calcrete development because its CL has a similar intensity to that of the calcrete and it post-dates the karst formation.

Discussion

There is a well developed sequence of cements at the top of the Gilwern Oolite. The sequence is most complete in the eastern portion of the outcrop, the earlier cements being absent further west. The inferred environments of precipitation of these cements are summarised in Fig. 2/1.

The micrite and fibrous cements are probably of marine origin, whereas the later cements are meteoric. This change is associated with the marine regression that resulted in the exposure of the top of the Gilwern Oolite. The absence of the earlier cements in the west is not unexpected since they were developed before the erosion surface that progressively removes more and more of the top of the oolite as one moves westwards. If these cements were ever present in the west any evidence of them has now been removed.

The meteoric cements record a change from phreatic to vadose conditions at the top of the Gilwern Oolite. The karst surface we see today cuts phreatic cements. No evidence of the vadose zone that must have once lain above these cements is seen; erosion associated with karst formation must have resulted in its removal. The lowering of the land surface associated with karst development has lead to the situation that exists today where the karst lies well below its original level, in fact, within what was once the phreatic zone below the karst at an earlier stage of its history. This is discussed further in Chapter 8.

The absence of rocks with abundant phreatic cements below the top 1–2 m. is a problem. It may be possible to explain this on textural grounds since the only samples that contain abundant phreatic cements are very pure oosparites. The ooids in these retain much of their original structure, unlike those from the impure oosparites lower down which are generally smaller and completely micritised. In the pure oosparites the first cement forms a dense, drusy rim around the ooids (Fig. 2/4c, e), whereas in the impure oosparites few cement crystals nucleate on the ooids. The ability of micritisation to prevent nucleation may be a result of the small size of the micrite crystals, alternatively it may reflect the presence of organic matter. Areas in which there are many calcite crystals growing will possess a larger surface area on which calcite can be precipitated and hence the pores will fill more quickly than pores which have few crystals growing in them. In the case in question the pores in the pure oosparite were often completely filled whereas the pores in the impure oosparite lower down still retained much porosity. Alternatively, the change in nucleation density could reflect a change in water chemistry with depth (Halley & Harris, 1969).

If the degree of cementation is only controlled by the nature of the substrate, the same cement zonation pattern should be seen in 'early' phreatic cements from both the pure and impure oosparites. This is the case for zone 2, but the non-luminescing calcite (zone 3) seen in the pure oosparite contains many brightly luminescing hairline subzones (Fig. 2/4c-f), far more, in fact, than are seen in the crystals in the impure oosparite. Unfortunately, initial 'late' calcite cement has a similar CL to zone 3. Unless a marker exists between 'early' and 'late' calcites with this sort of CL, as in Fig. 2/5i,j, they cannot be told apart. Such markers are extremely rare. Therefore it is impossible to be sure that the zone 3 calcites in the pure oosparite are not present in the impure oosparite also.

Although the precipitation of meniscus cement was associated with the introduction of abundant clay during exposure, CL suggests that the meniscus cements were not precipitated from the same groundwaters as the calcrete, since they are non-luminescing whereas the calcrete and the sparry cement associated with it are brightly luminescing. The meniscus cements probably pre-date the calcrete as they are often overlain by more clay. The water table at this time seems to have been at the level of the fissure zone in the Clydach area, since this is the limit of vadose cementation and clay penetration. This is in agreement with the interpretation of Wright (1980, 1981, 1982).

The brecciation of the top of the Gilwern Oolite is associated with karstification and post-dates phreatic cementation.

'Early' cementation in the remainder of the Oolite Group

a. Within the remainder of the Gilwern Oolite

Evidence that 'early' cementation has occurred in the remainder of the Gilwern Oolite includes:-

1. sculptured, intraformational erosion surfaces;
2. intraclasts;
3. diagenetic sediment;
4. cements with fabrics typical of early cementation.

These criteria are discussed below.

Sculptured, intraformational erosion surfaces

These surfaces are highly irregular, with overhanging edges and holes (Fig. 2/6). They have a relief of 15 cm. or more and in some cases probably have a lateral extent in excess of ½ km. They are the result of erosion of cemented sediments, for unconsolidated sediment could not retain such intricate shapes. These surfaces are not obvious in outcrop unless they separate two very different rock types, i.e. pelsparite and biosparite. Two surfaces were sampled unwittingly and were only identified on cut and ground surfaces so there is the possibility that more exist. There was no sign of encrustation or boring of these surfaces either on a hand

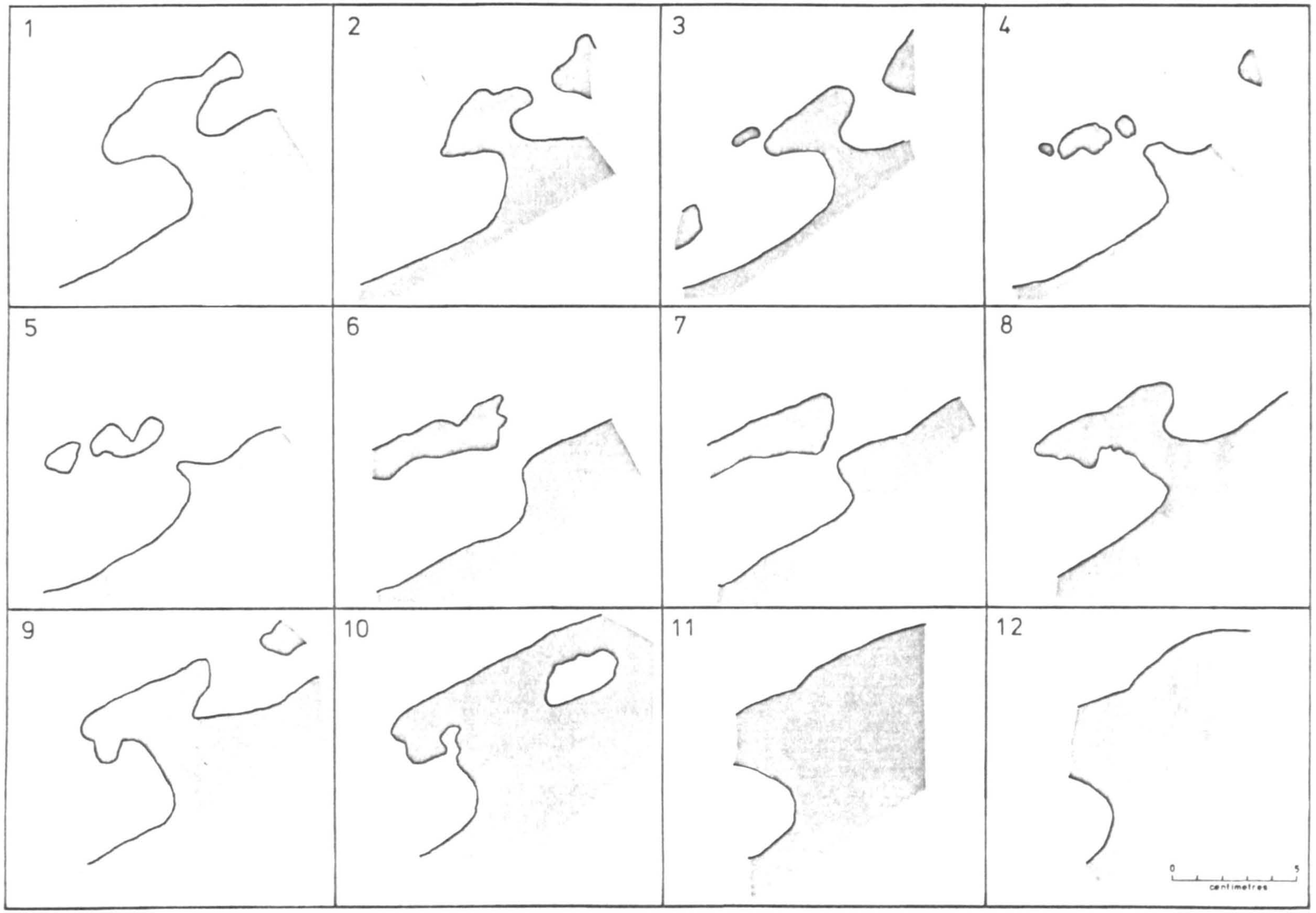


Fig.2/6 AN EROSION SURFACE WITHIN THE GILWERN OOLITE

Serial sections through the erosion surface found in Sample 18337, taken at approx. ½cm. intervals. Shading indicates the area below the erosion surface.

specimen or outcrop scale. The three surfaces found will be described below and an attempt made to identify the cements responsible for their 'early' lithification.

SAMPLE 18337, Coral Bed, Pwll du

This is the surface illustrated in serial section in Fig. 2/6. It separates an oobiosparite above from an oopelsparite below. Coarse bioclastic debris is concentrated immediately above the surface. The surface cuts sedimentary laminations in the pelsparite. Although the surface is a very noticable feature in slabs, it is diffuse and hard to recognise in thin section. This is because the surface is not micritised and grains are not obviously cut.

Above the surface, cementation is by faintly ferroan calcite which has a dull luminescence, followed by calcite which is non-luminescing but contains brightly luminescing, harline subzones (Fig. 2/7a). Syntaxial overgrowths have an earlier inclusion-rich calcite zone. In ooid-rich areas below the surface, exactly the same cements are present (Fig. 2/7b). In pellet-rich areas the pores are too small to positively identify the cements, but it appears to contain many inclusions, giving it a brown tinge. CL shows it to be non-luminescing except for irregular patches which are brightly luminescing. The inclusion-rich syntaxial overgrowths above the surface have a similar CL, although the bright patches (probably filled solution vugs, see Chapter 3) do not appear to be so abundant here

SAMPLE 21661, Coral Bed, Twyn-y- dinas

This surface is clearly visible in outcrop, and possibly equivalent junction is found at Craig y Gaer. A pelsparite is overlain by a coarse pelbiosparite. This junction is

Fig.2/7 'EARLY' CEMENTS FROM WITHIN THE GILWERN OOLITE

a) Cement from above the erosion surface identified at Pwll du. The first cement is ferroan and dull luminescing (A). Sample 18337.

b) Cement from below the erosion surface identified at Pwll du. The first cement is ferroan and dull luminescing (A). Later cements are non-luminescing but contain many brightly luminescing, hairline subzones. Sample 18337.

c) Cement from above the erosion surface identified at Daren Ddu. There is an initial dull luminescing zone (arrow) followed by non-luminescing calcite. Sample 17856.

d) Cement from below the erosion surface identified at Daren Ddu. There is an initial dull luminescing zone followed by non-luminescing calcite. Sample 17856.

e) Transmitted light photomicrograph showing ooids cut by the erosion surface identified at Daren Ddu. A thin isopachous rim of cement around the ooids is also cut by the surface (arrow). Sample 17856.

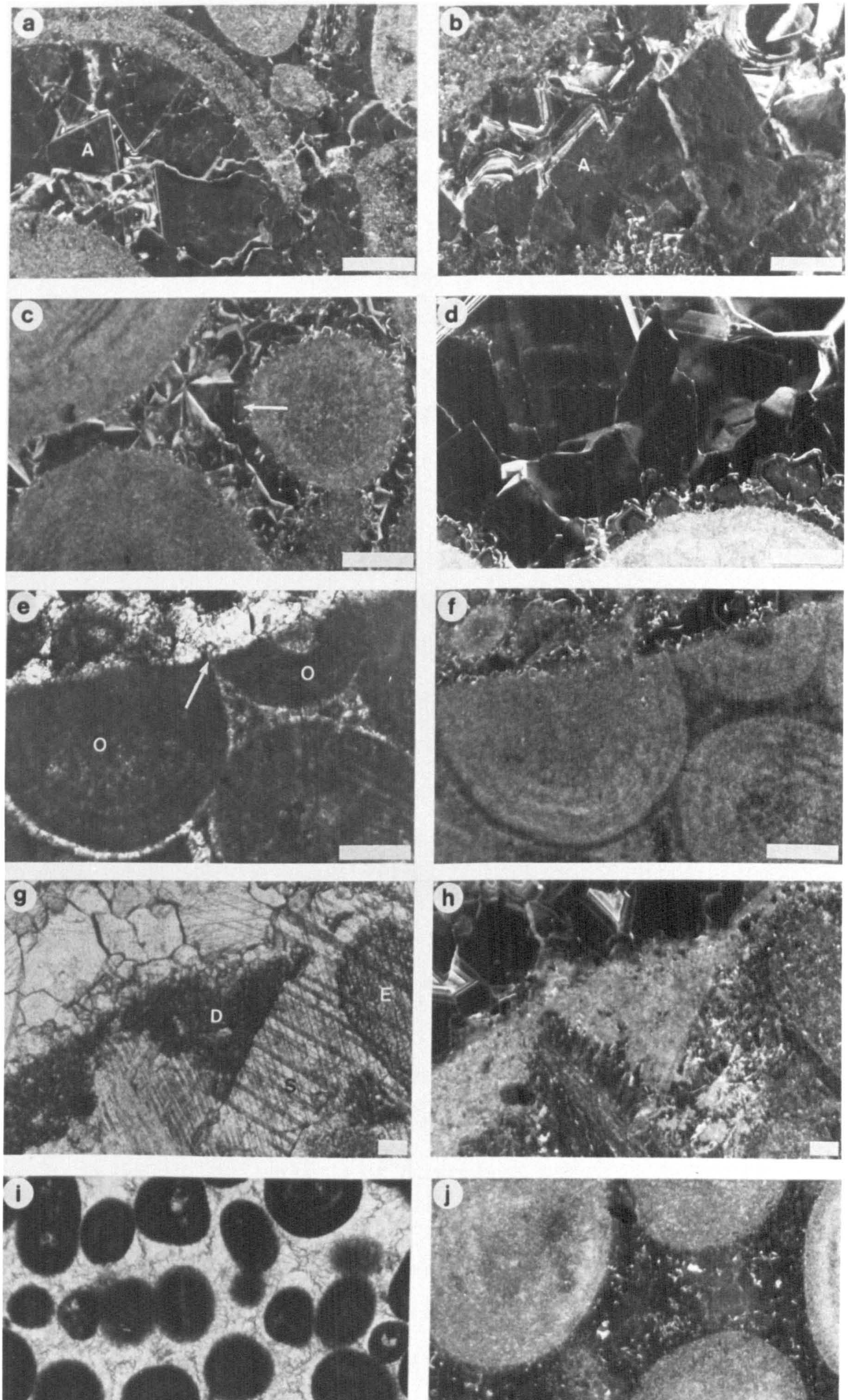
f) The same area as shown in (e). The isopachous rim is non-luminescing. Sample 17856.

g) Transmitted light photomicrograph showing diagenetic sediment (D) overlying an inclusion-rich syntaxial overgrowth (S) on an echinoderm fragment (E). Sample 17853.

h) The same area as shown in (g). Note the patchy luminescence of the syntaxial overgrowth. Sample 17853.

i) Transmitted light photomicrograph showing fibrous cements displaying polygonal sutures. Sample 20562.

j) Fibrous cement is dominantly non-luminescing, but contains patches of brightly luminescing material. Sample 20562.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stylolitised along much of its length. Much detrital quartz is concentrated along it. Sedimentary laminations within the pelsparite are cut by the surface.

The intergranular areas within the pelsparite are very small, making it impossible to identify the cement. CL reveals it to be non-luminescing except for irregular, brightly luminescing patches. Similar areas are found within the echinoderm plates and earliest syntaxial overgrowths above the surface. As in the case of the previous sample, there is no apparent difference in the cements above and below the erosion surface.

SAMPLE 17856, middle of the Gilwern Oolite, Daren Ddu

This surface separates impure ossparite above from pure oosparite below and not surprisingly is obscure in outcrop. It is best seen at the north end of the Daren Ddu Quarries, where it can be traced the whole length of the quarry (approx. 16 m.) It can also be found at Craig y Gaer and possibly at the southern end of the Daren Ddu Quarries. It has not been found at Llanelly Quarry. The shape of the surface is similar to that described from 18337 (Fig. 2/6) but in this instance it is micritised. At one point in the sample the surface is broken and a fissure extends several millimetres below the surface clearly cutting the grains. This may be a boring, but there is no evidence of extensive boring or encrustation of the surface.

The pure oosparite below the surface is almost entirely cemented by non-ferroan calcite, whereas there is a far higher proportion of later ferroan calcite above the surface. This is a situation similar to that described for the sparry, phreatic cements at the top of the Gilwern Oolite. In both cases this does not mean that there are different cements above and below the surface as is made clear with CL (Fig. 2/7c, d). The only cement that can be identified below the surface, but not above, is an exceedingly thin isophachous rim (5-10 µm thick). It is only visible where it is covered by micritic diagenetic sediment (Fig. 2/7a). It appears to be non-luminescing (Fig. 2/7f).

It has proved remarkably difficult to identify the 'early' cements responsible for the lithification of the sediment associated with the erosional surfaces. In only one case, 17856, has such a cement been positively identified and even here it is only present in miniscule quantities. Possible reasons why 'early' cement is impossible to identify within the Coral Bed are:-

1. only very small amounts of cement are needed to lithify sediment sufficiently for intricate erosion surfaces to develop (as is evident from 17856). The pores are so small in the pelsparites below the erosion surfaces in the Coral Bed that it may just not be possible to see these cements with the methods employed;
2. similar cements developed contemporaneously with sedimentation both above and below the erosion surfaces. Hence, the distribution of pre-erosion cement is not unique to the lower unit.

The morphology of the erosion surfaces described above is similar to erosion surfaces described by Ginsburg (1953) and Read & Grover (1977), which they interpreted as being the result of intertidal erosion. A similar origin is envisaged for the intricate erosion surfaces from the Gilwern Oolite.

Intraclasts

The abundance and size of intraclasts varies within the Gilwern Oolite. Fig. 2/8 illustrates this variation in the Clydach area. At the west end of the outcrop, where only the base of the sequence is represented, intraclasts are rare.

In the Clydach area there is an increase in the size and abundance of intraclasts in the middle of the Gilwern Oolite. This occurs close to the level at which the erosion surfaces are found at Daren Odu. It has been suggested that the erosion surfaces formed in the intertidal zone. If the intraclasts were locally derived, as seems likely, their increased size and abundance may reflect the shoaling and associated increase in erosion that resulted when this area was raised to near sea-level.

Not surprisingly most of the intraclasts found immediately above the erosion surface at Daren Odu look very similar to the sediments immediately below the surface and show the same very thin isopachous rim. Intraclasts from elsewhere vary greatly in lithology, with varying proportions of ooids, pellets and bioclasts. Many of the clasts have their pores completely filled with micrite: this may be a cement or an internal sediment. Sparry calcite cements can be matched with the cements in the surrounding sediment. The margins of intraclasts are usually well rounded and grains at the edges are truncated. Often the outer 100 μm. or so is micritised. Occasionally the centres of the intraclasts have fallen

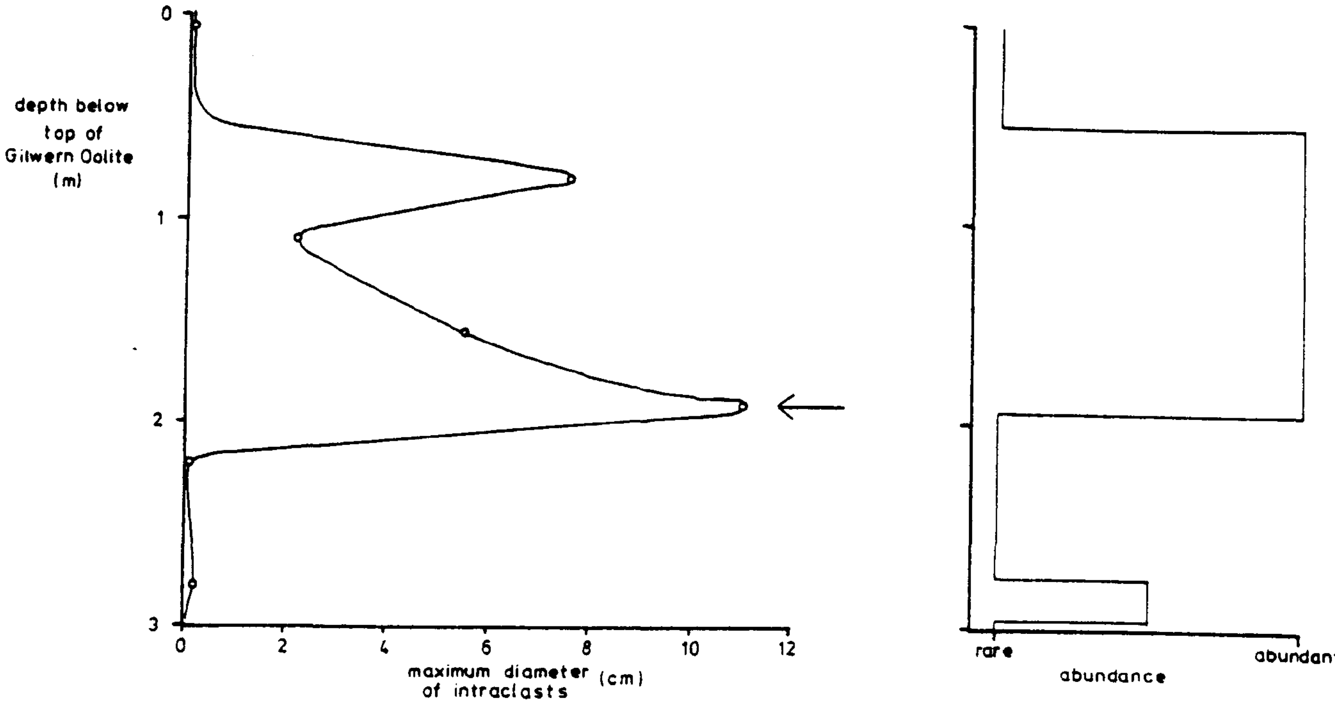


Fig.2/8 THE DISTRIBUTION OF INTRACLASTS WITHIN THE GILWERN OOLITE

Variation in the size(a) and the abundance(b) of intraclasts found within the Gilwern Oolite, above the Coral Bed, in the Clydach area. The arrow in (a) indicates the level at which the erosion surface occurs at Daren Ddu.

out and been filled by later cement; the margins are preserved since they have been micritised. This illustrates how poorly cemented some of the intraclasts were when they were incorporated into the sediment.

Diagenetic sediment

'Early' internal sedimentation is rare in the Gilwern Oolite. Only one example has been found, which is from the Coral Bed at Daren Ddu. Carbonate diagenetic sediment overlies an inclusion-rich syntaxial overgrowth on an echinoderm fragment (Fig. 2/7g, h). Ferroan calcite overlies the diagenetic sediment. This suggests that the syntaxial overgrowth formed very early.

Typical 'early' cements

Cements that fall into this category are rare in the Gilwern Oolite. Cements reminiscent of marine, phreatic cements are occasionally found. These have fabrics very similar to those described by Dravis (1979) for oolitic hardgrounds (Fig. 2/7i). Cemented layers are not found though. The cement is restricted to small, irregular patches with no distinctive margins. In one case it is only found within the sediment within an articulated shell. Obviously the right physical and/or chemical environment for this type of cementation was rarely attained. The only examples of this type of cementation are found from Coed Pant-y-daren westwards.

These cements are non-luminescing, but are mottled with dull luminescing patches (Fig. 2/7j). They appear to be similar to associated inclusion-rich syntaxial overgrowths. Assuming that the fibrous Carboniferous marine cements were like recent ones, this may reflect a change in mineralogy from aragonite or high-Mg calcite to low-Mg calcite.

b. Within the Clydach Beds

Evidence of 'early' cementation is rare in the Clydach Beds. This is in part due to their fine grained nature, micrites and pelsparites predominating, which makes the application of the criteria for the recognition of 'early' cements impossible to apply with the methods of investigation employed, and partly because much of the Clydach Beds are dolomitised. The presence of micrite crusts in the west indicates that at least part of the outcrop was subaerially exposed, pene-contemporaneously, which would make 'early' meteoric cementation a distinct possibility. Unfortunately the rocks underlying the crusts are pelmicrites, so no evidence of any 'early' cementation can be identified. Two pieces of information that do illustrate that 'early' cementation was occurring are:

1. intraclasts;
2. diagenetic sediment.

Intraclasts

Unfortunately all intraclasts found are micrites or biomicrites, very similar to the rocks exposed in the Clydach Beds themselves. There is no possibility of identifying the cements in these with the methods of investigation employed here. However, the presence of abundant, rounded intra-clasts within the Clydach Beds (Fig. 2/9a) does suggest that 'early' cementation was occurring.

Fig.2/9 EVIDENCE OF 'EARLY' CEMENTATION IN THE CLYDACH BEDS, BLAEN ONNEU OOLITE AND THE DAREN DDU BEDS

a) Transmitted light photomicrograph showing intraclasts (I) surrounded by geopetal internal sediment (M) and sparry calcite (S). Sample 20560.

b) Diagenetic sediment (D) overlying sparry calcite crystals. The final cement is 'late' ferroan calcite (Fe). Sample 18335.

c) Ooids with initial non-luminescing cement. By analogue with other cements these are thought to be 'early'. Sample 17841.

d) Internal sediment (D) lying directly on a brachiopod fragment (B). The cavity below the brachiopod is filled with zoned calcite cement. Sample 17886

e) Transmitted light photomicrograph showing diagenetic sediment (D) overlying an inclusion-rich syntaxial overgrowth (S) on an echinoderm fragment (E). Sample 17886.

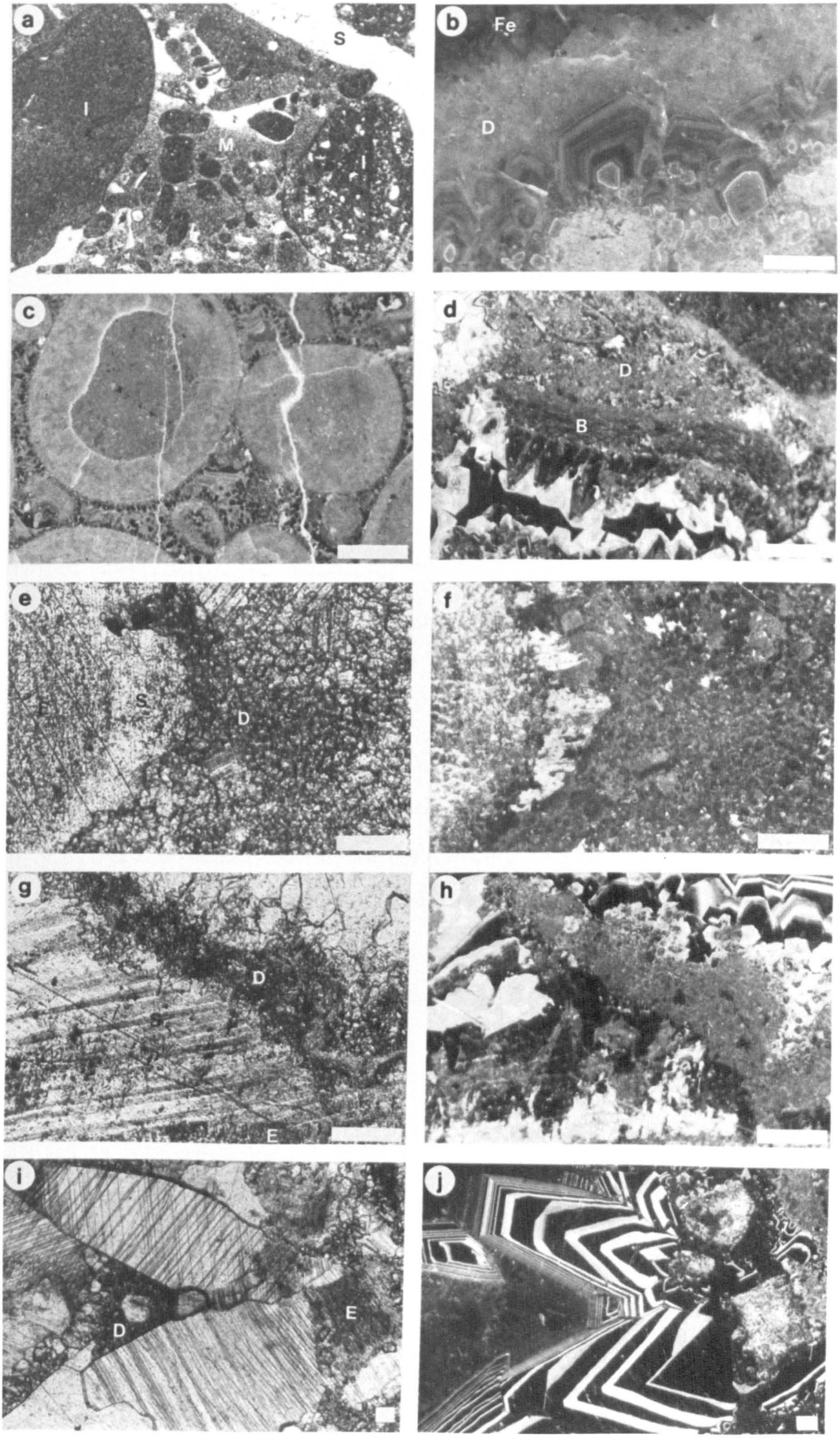
f) The same area as shown in (e). Note the patchy luminescence of the syntaxial overgrowth. Sample 17886.

g) Transmitted light photomicrograph showing diagenetic sediment (D) overlying inclusion-rich syntaxial overgrowth (S). Sample 17886.

h) The same area as shown in (g). Note the patchy luminescence of the inclusion-rich syntaxial overgrowth. Sample 17886.

i) Transmitted light photomicrograph showing diagenetic sediment (D) overlying sparry calcite crystals. Sample 17886.

j) The same area as shown in (i). This is the only sample where sparry calcite showing this CL pattern is found. Sample 17886.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Diagenetic sediment

Although diagenetic sediments usually do not overlie cement this does occasionally happen (Fig. 2/9b). The cement involved is very faintly ferroan and has a CL unlike any found elsewhere in the Oolite Group; it is dull to bright and shows zonation.

c. <u>Within the Blaen Onneu Oolite</u>

There is only rare, scattered evidence of 'early' cementation in the Blaen Onneu Oolite. This is in the form of:

1. intraclasts;
2. diagenetic sediment;
3. CL cement fabrics similar to those of known 'early' cements.

Intraclasts

The only intraclast found is well rounded, consisting of a relatively pure oosparite (17872). A thin, isopachous rim of cement surrounds the grains, similar to that described in sample 17856. This is not present outside the clast. Especially near the intraclast's margin, the isopachous rim is overlain by micrite which assists in its recognition. As in the case of 17856 it is difficult to identify the isopachous rim using CL. It is probably at most only dully luminescing, similar to that of 17856 (Fig. 2/7d). Later sparry cements, within the clast, are identical to those in the surrounding sediment.

Diagenetic sediment

Diagenetic sediment is only found in sample 17887 where it overlies inclusion-rich syntaxial overgrowths.

CL cement fabrics similar to those of known 'early' cements

The first cement in sample 17841 (Fig. 2/9c) has a CL character very similar to that of the original cements found in sample 21657 (Fig. 2/2g). There is no other evidence as to the age of this cement. Presuming that the similarity is due to similar environments of precipitation this cement may be 'early'.

d. Within the Daren Ddu Beds

It is only possible to study the cements of the Daren Ddu beds at the west end of the outcrop; further east they are very fine grained and largely dolomitised. There is virtually no evidence of 'early' cementation except in the biosparites directly overlying the Pwll-y-cwm Oolite at Chaw Pant-y-Rhiw (samples 17885, 6). Within these biosparites many episodes of diagenetic sedimentation are found. The biosparites are unusual in that they contain authigenic glauconite, indicating low sedimentation rates. Therefore, it would be possible to introduce many generations of diagenetic sediment from the sediment-water interface.

Internal sediment is found lying directly on allochems (Fig. 2/9d) as well as diagenetic sediment overlying cement (Fig. 2/9e, f, g, h). Large sparry calcites are found filling some of the bigger voids; these are also overlain by diagenetic sediment (Fig. 2/9i, j). The calcite overlying this diagenetic sediment can positively be identified as 'late' (see 2.2).

The 'early' cements have a very distinctive CL which cannot be correlated vertically and only dubiously horizontally

(Fig. 2/9d, f, h, j). The inclusion-rich syntaxial overgrowths have a typical patchy and variable CL (Fig. 2/9f, h), similar to that found in inclusion-rich syntaxial overgrowths elsewhere.

e. <u>Within the Pwll-y-cwm Oolite</u>

'Early' cements have been identified within this oolite on the basis of:

1. diagenetic sediment;
2. fabrics typical of early cements;
3. CL fabrics similar to known 'early' cements.

Diagenetic sediment

Sample 17846, from within the Pwll-y-cwm Oolite at the western end of the outcrop, is one of several samples that contain diagenetic sediment overlying isopachous rims around ooids (Fig. 2/10a, b). Ofen the rim is too small to study in detail, but in one case it could be correlated with the inclusion-rich stage of a syntaxial overgrowth (Fig. 2/10c, d). In most cases the rims show patchy, dull luminescence (Fig. 2/10b, d), but occasionally they are very brightly luminescing. Well developed, non-luminescing fibres are occasionally seen radiating from some ooids (Fig. 2/10e), with average dimensions of 3 µm by 1 µm (c.f. fibrous cements at the top of the Gilwern Oolite, Fig. 2/2g). Equivalent syntaxial overgrowths have spires that have the same irregular luminescence (Fig. 2/10d).

Fabrics typical of early cements

Allochems at the top of the Pwll-y-cwm Oolite at Chaw Pant-y-rhiw are cemented by isopachous, fibrous (?)

Fig.2/10 'EARLY' CEMENTS IN THE PWLL-Y-CWM OOLITE

a)Transmitted light photomicrograph showing diagenetic sediment (D) overlying fibrous cement (F) on ooids (O).Sample 17846.

b)The same area as shown in (a).Note the patchy luminescence of the fibrous cement.Sample 17846.

c)Transmitted light photomicrograph showing diagenetic sediment (D) overlying an inclusion-rich syntaxial overgrowth (S).Sample 17846.

d)The same area as shown in (c).Note the patchy luminescence of the syntaxial overgrowth.Sample 17846.

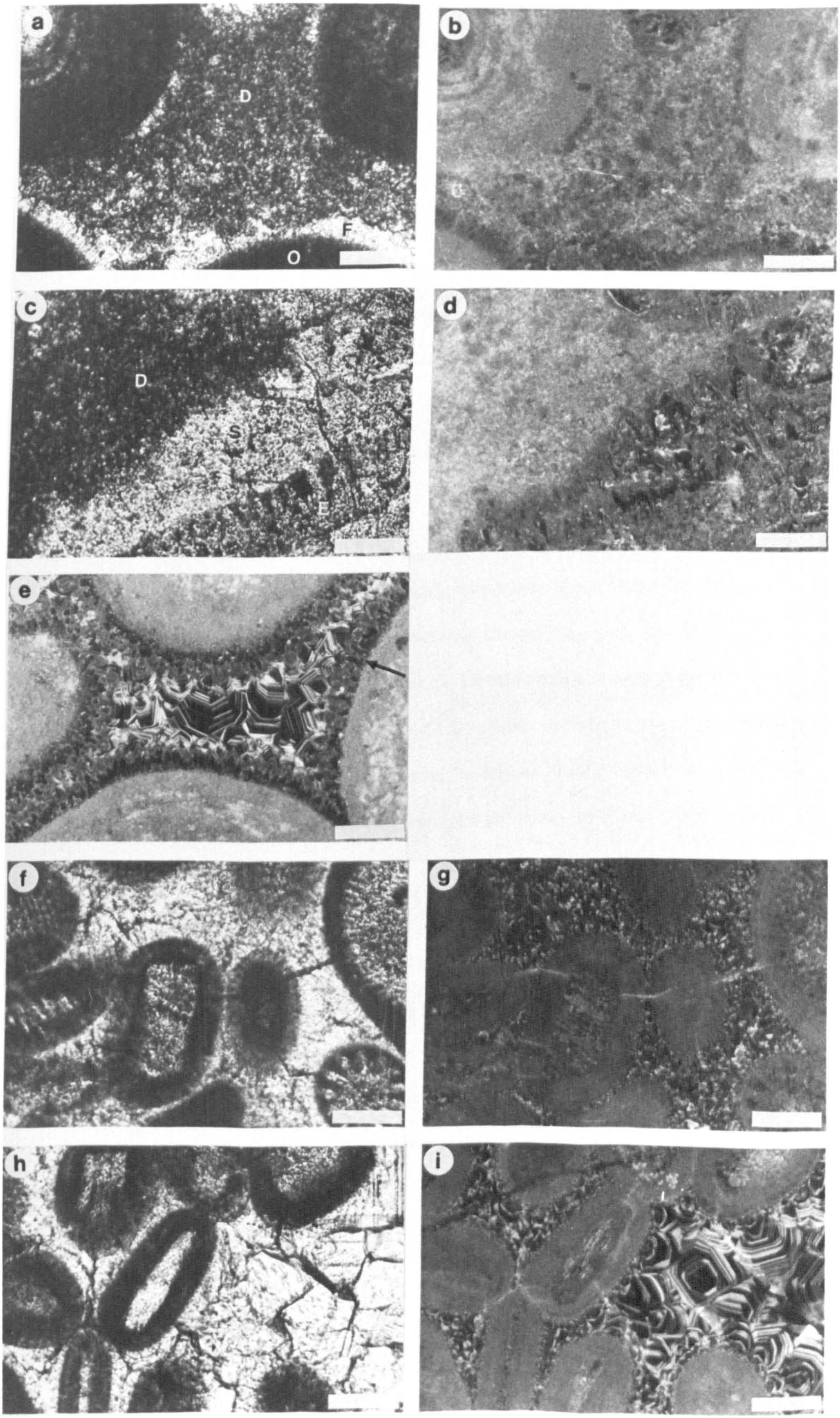
e)The original fabric is preserved in some fibrous rims and is seen to consist of non-luminescing crystals.Some of these are parallel-sided (arrow).Sample 17846.

f)Transmitted light photomicrograph showing fibrous cement from the very top of the Pwll-y-cwm Oolite.Sample 21659.

g)The same area as shown in (f).Note the patchy luminescence of the fibrous cement.Sample 21659.

h)Transmitted light photomicrograph showing cement from several centimetres below the top of the Pwll-y-cwm Oolite.Here it is sparry.Sample 21659.

i)The same area as shown in (h).The sparry calcite shows regular zonation. Sample 21659.



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cements (Fig. 2/10f, g). This cement decreases rapidly in abundance away from the top of the oolite and has disappeared 1 cm. below the top. Here sparry cement fills the pores (Fig. 2/10h, i). The isopachous cements have a brown tinge suggesting that they contain may inclusions. Contemporary syntaxial overgrowths on echinoderm plates are also rich in inclusions. In places the irregular top of the oolite cuts down below the level of the isopachous cements and here the pores near to the surface are filled with internal sediment, there being no cement.

The isopachous cements have a very irregular luminescence, as do the equivalent syntaxial overgrowths (Fig. 2/10b). The cements are basically non-luminescing, but contain brightly luminescing patches. In syntaxial overgrowths this occasionally forms a zone outside the non-luminescing area. Syntaxial overgrowths, showing similar luminescing character, are found even where the isopachous rims are not developed around the ooids.

Isopachous, fibrous cements have been described from elsewhere in the Oolite group and a marine origin attributed to them. This also implies a marine origin for the inclusion-rich syntaxial overgrowths. The decrease in the amount of this cement downwards is reminiscent of the distribution one would expect for a **hardground** (Dravis, 1979). However, there is no sign of encrusting organisms on the top of the oolite, although there are steep-sided pits, described in Chapter 1, which could be interpreted as borings. Unfortunately other samples collected from the top of the Pwll-y-cum Oolite do not contain the top few centimetres and so are below the level where one would expect the hardground cements to be developed.

CL cement fabrics similar to known 'early' cements

One example of such a cement has already been described from the Pwll-y-cwm Oolite and is illustrated in Fig. 2/10e. Other examples are from the eastern portion of the outcrop, close to the example described from the Blaen Onneu Oolite (Fig. 2/9c). Here the crystals are non-luminescing and often show sharp terminations.

These look very similar to marine, fibrous cements previously described. There is no direct evidence as to their age.

Conclusions

From the account of 'early' cements given above several observations can be made:

1. despite abundant evidence of subaerial exposure in the form of karsts, calcretes and micrite crusts there is very little indication of 'early' meteoric cementation. Indeed, it is largely limited to the very top of the Gilwern Oolite;
2. there is abundant evidence for the 'early' age of inclusion-rich syntaxial overgrowths from most units of the Oolite Group. Much of this evidence is provided by the presence of diagenetic sediment overlying these cements. The syntaxial overgrowths in these situations are not thought to be the result of neomorphic replacement of internal sediment (Bathurst, 1975 p. 492), since they are identical to the majority of the inclusion-rich syntaxial overgrowths which show no association with internal sediment.

The similarity of this cement throughout the Oolite Group is thought to reflect the fact that it developed contemporaneously with sedimentation in very similar environments. It is not thought to represent a single precipitation event occurring after the Oolite Group had been deposited. The equivalence of the inclusion-rich syntaxial overgrowths to isopachous fibrous cements suggests they have a marine origin. The irregular CL that is typical of these cements is discussed in Chapter 3;

3. cements precipitated at different times but in similar environments tend to have similar CL characteristics. This is illustrated by the inclusion-rich syntaxial overgrowths;
4. cements that are very limited in their distribution (as shown by CL) have generally been identified as 'early';
5. fibrous cements are usually greatly altered, although occasionally what are presumed to be their original internal structure is, at least in part, preserved and is visible using CL. Where it can still be seen it consists of prismatic crystals several microns long and a micron wide. These are non-luminescing. The poor preservation of the original structure is thought to reflect the unstable nature of the original minerallogy during freshwater diagenesis.

2.2 'Late' cementation

Cements that were precipitated after the exposure of the top of the Gilwern Oolite have been termed 'late'. The criteria used to identify these cements are listed below:

1. cements that fill fractures in the calcrete must post-date calcrete formation (Fig. 2/11a); earlier fractures are filled with calcrete-like material;
2. cements that overlie pore fillings that are interpreted as being synchronous or penecontemporaneous with calcrete formation must be 'late';
3. the presence of markerswithin a cement sequence which are associated with calcrete formation can be used to separate 'early' from 'late' cement (Fig. 2/5j). These markers consist of etched surfaces or layers of brightly luminescing calcite. However, these tend only to occur at the top of the Gilwern Oolite;
4. cements that can be correlated, through distinctive staining and/or CL patterns, with cements that are known to be 'late' from the above criteria or with cements from formations overlying the Oolite Group (Fig. 2/11b-e) must themselves be 'late'.

Using the above criteria the following sequence of 'late' cements has been identified:

1. predominantly non-luminescing calcite. This contains fine, brightly luminescing lines;
2. faintly ferroan calcite (at least inthe case of 22361) which is brightly luminescing and shows slight zonation;
3. zoned ferroan calcite which has dull luminescence, the zones of which have slightly different CL tones;
4. baroque dolomite which is non-luminescing.

The above divisions of the 'late' cements are discussed further in 2.3 where they are fitted into a general zonation scheme.

Fig.2/11 'LATE' CEMENTS

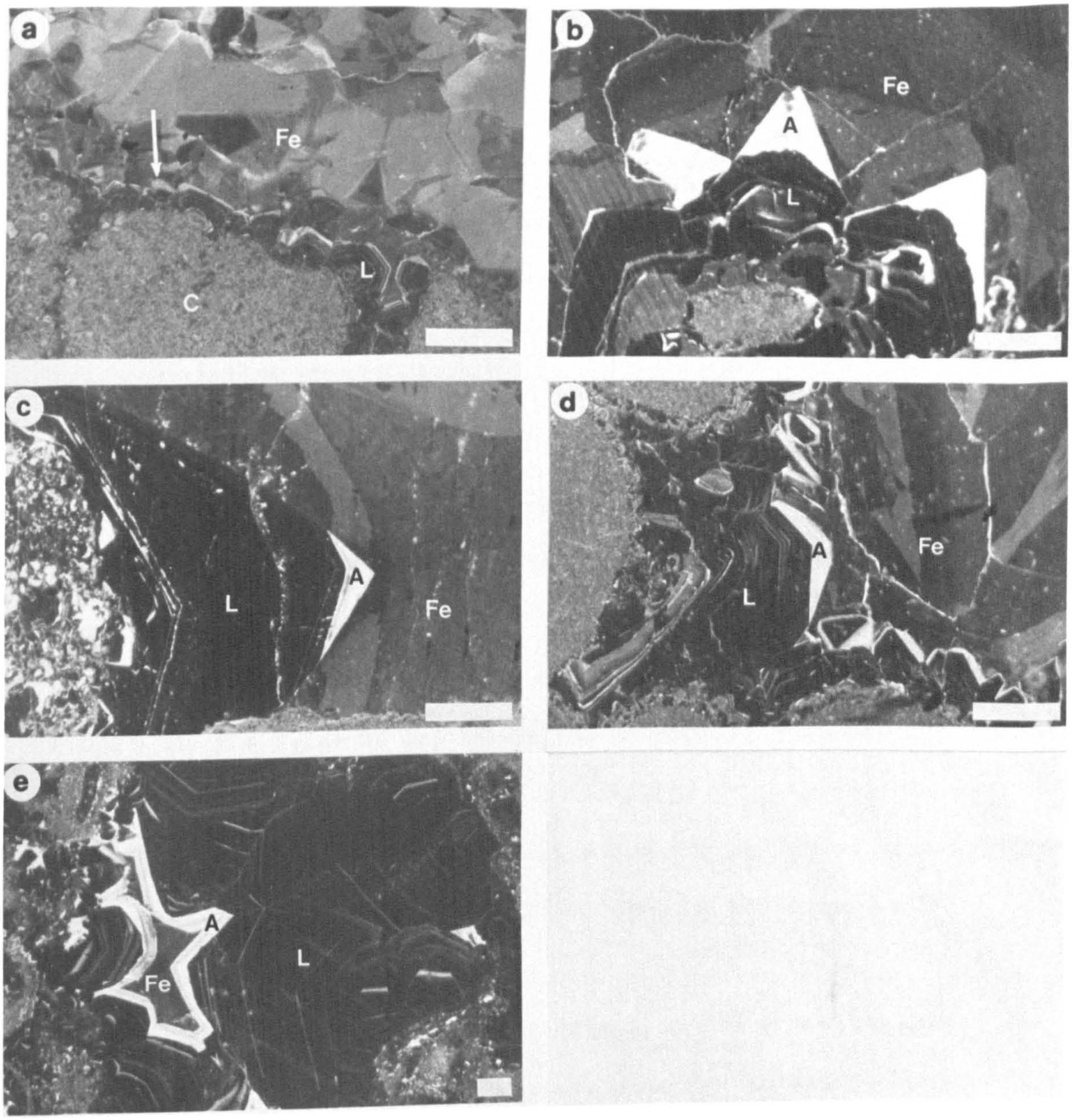
a) Cement filling a fracture cavity in calcrete (C). The dull luminescing area (Fe) is ferroan and the non-luminescing area with fine, brightly luminescing lines (L) is non-ferroan. A thin layer of brightly luminescing calcite separates the two (arrow). Sample 17843.

b) Cements from the base of the Penllwyn Oolite, Llanelly Fm. Brightly luminescing calcite (A) lies between predominantly non-luminescing calcite (L) and dull luminescing ferroan calcite (Fe). Sample LX14 of V.P. Wright.

c) Cement from the Cheltenham Limestone Member, Llanelly Fm. The same sequence of cements are present as described in (b). Sample 1-17.

d) Cement from the top of the Gilwern Oolite. A similar series of cements are present as described from the Llanelly Fm. in (b) and (c). Sample 17823.

e) Cements from the Gilwern Oolite. A similar series of cements are present as described from the Llanelly Fm. in (b) and (c). Sample 20539.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Fe
L

The 'late' cements also occur within the Llanelly Formation and therefore must be younger than the sedimentation of this formation. Further than this there is no evidence available at the present time to date these cements more accurately.

2.3 Correlation of cement zones

The importance and implication of being able to correlate cement zones was first pointed out by Evamy (1969). Since then several correlation schemes, using CL as a basis of zone identification, have been documented (Ebers & Kopp, 1972; Oglesby, 1976), the most far reaching being that of Meyers (1974, 1978). Meyers (1978) was the first to introduce the concept of 'cement stratigraphy' which requires the ability not only to correlate cements but also date their precipitation and recognise such features as unconformity surfaces within them; drawing analogues with lithostratigraphy.

It has proved possible to correlate cement zones through much of the Oolite Group in the study area and indeed further westwards, since the same zones have been identified in samples from Cwar y Ystrad, 5 km. west of Blaen Onneu. The identification of the same zones further eastwards is limited by the dolomitisation that occurs in that direction. Some of the cement zones identified have been mentioned in 2.1 and 2.2. These and the other zones are fitted into a cement zonal scheme outlined below.

What is meant by a 'cement zone'?

Before going further it is necessary to define what is meant by 'zone' in the context of cement stratigraphy. A cement zone must be easily identifiable using either staining and/or CL techniques. In the case of the Oolite Group, cement zones were intially identified on the basis of staining since isotope sampling was done from stained thin sections. However, it became apparent that the zones identified in this way also had a characteristic CL pattern.

Fig. 2/12a illustrates zoned calcite. However, this shows only part of a crystal. If a larger portion of the same crystal is considered (Fig. 2/12b) it can be seen that the zones illustrated in Fig. 2/12a are part of a zone in a larger scale zonation pattern. This zone is itself part of an even larger scale zonation pattern (Fig. 2/12c). Therefore, one can have zoned zones and zoned, zoned zones and so on. It is the largest scale variation that, in the Oolite Group, corresponds to the staining pattern and it is the largest scale zones that are considered as 'cement zones'. These can be correlated within the Oolite Group. Simply, a 'cement zone' is an area within which the staining and/or CL is fairly constant. This interpretation agrees with that of Meyers (1974, 1978).

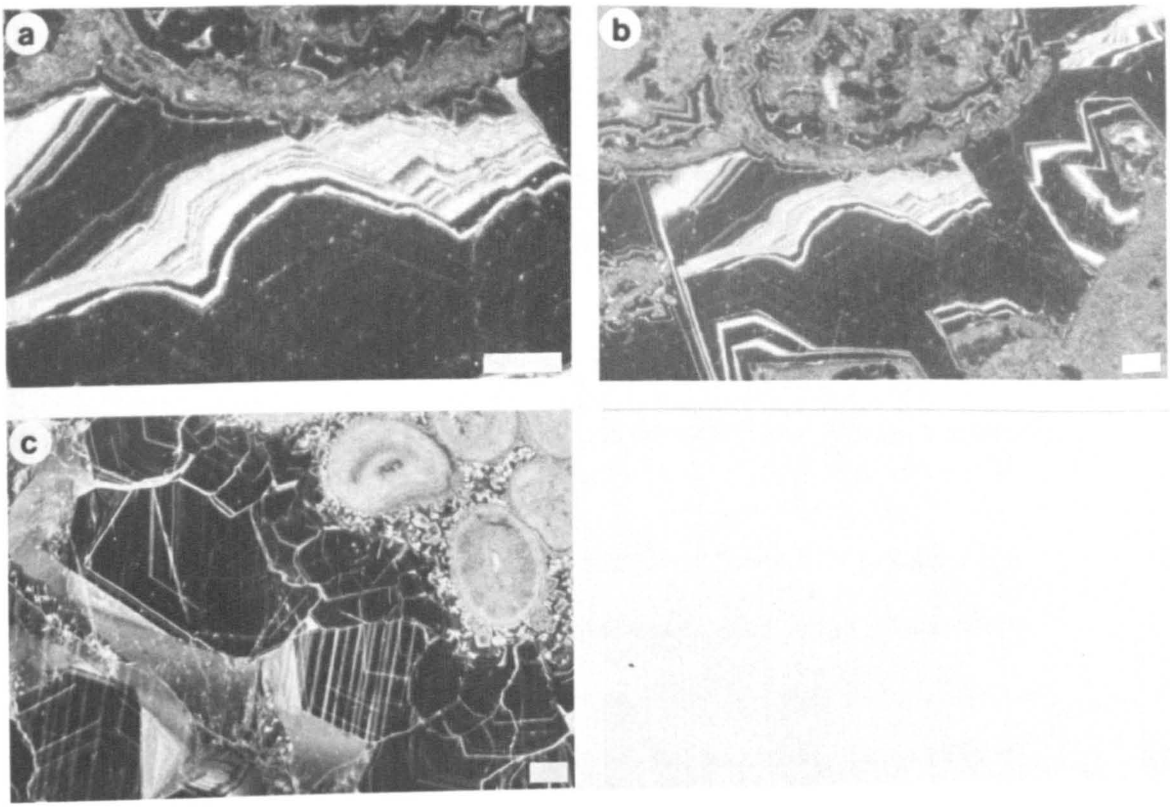
The different scales on which zonation can occur can easily lead to misunderstanding and confusion when considering the subdivision of cements into zones. Therefore, a terminology is required that immediately makes it clear on what scale zonation is being discussed. One possibility is to divide cement zones into subzones. This is only a bipartite division and since subzones may themselves be zoned it is considered to be inadequate. The following open-ended system is preferred. The cement zone is considered to be a first order zone. This is sub-divided into second order zones and these into third order zones and so on. In practice it is unlikely that more than a four-fold division would be needed.

Fig.2/12 VARIOUS SCALES OF CEMENT ZONATION

a) Zoned calcite consists of brightly and non-luminescing calcite. The brightly luminescing calcite is itself zoned. Sample 17905.

b) The area shown in (a) is shown in the box. The zoned calcite shown in (a) is itself a zone in a larger scale zonation pattern. Sample 17905.

c) The zones illustrated in (b) are the brightly luminescing hairlines closest to the allochems. These zones form part of a larger scale zonation pattern. Sample 17905.


a
b
c

Another problem with cement zones is how much variation to allow within a first order zone before two separate first order zones can be identified. Too rigorous a limitation cannot be applied for the following reasons:

1. variation within a zone is to be expected and is the result of the nature of the cementation process. This is discussed later in this section;
2. the CL seen will vary with the instrument and working conditions used. Photographs will vary with equipment, processing, exposure time etc. Variations will also exist between observers, since CL can only be described quantitatively.

The cement zonal scheme

The first order zones that have been identified are described below. These are illustrated in Fig. 2/13-15. It is impossible to illustrate an isolated zone, but an attempt has been made to group the illustrations to highlight various features of specific zones.

Zone 1

This consists of inclusion-rich syntaxial overgrowths on echinoderm and brachiopod fragments. It is strongly ferroan. It is non-luminescing although it often contains irregular patches with dull to bright luminescence in three or four tones. Very brightly luminescing spots correspond to brown inclusions of unknown origin. An irregular, dull luminescing area is visible between the echinoderm plate and Zone 1 in Fig. 2/13c. This is also ferroan. Similar areas are present in other samples although they may be overlain by Zone 2a rather than Zone 1 (Fig. 2/13d). In view of its unusual distribution the origin of this calcite

Fig.2/13 ZONE 1,2a,2b AND 3 CEMENTS

a)Syntaxial overgrowth containing Zones 1,2b and 6.Sample 17841.

b)Syntaxial overgrowth containing Zones 1,2b and 6.Zone 1 is basically non-luminescing but contains patches of luminescing calcite.Sample 18313.

c)Syntaxial overgrowth containing Zones 1 and 2b.An irregular,dull luminescing area lies between Zone 1 and the substrate.It consists of elongate areas extended perpendicular to the substrate.This has been called 'poorly defined' Zone 1 (1?).Sample 17841.

d)An irregular,dull luminescing area lies between the substrate and Zone 2a calcite.This is 'poorly defined' Zone 1 (1?).It consists of two types of calcite that can be identified as two distinct ferroan calcites by staining, the lighter of the two calcites appears to overlie the duller one.Sample 17872.

e)Syntaxial overgrowth containing Zones 2a,2b,3 and 4.Zone 2a has a typical patchy luminescence.Sample 17869.

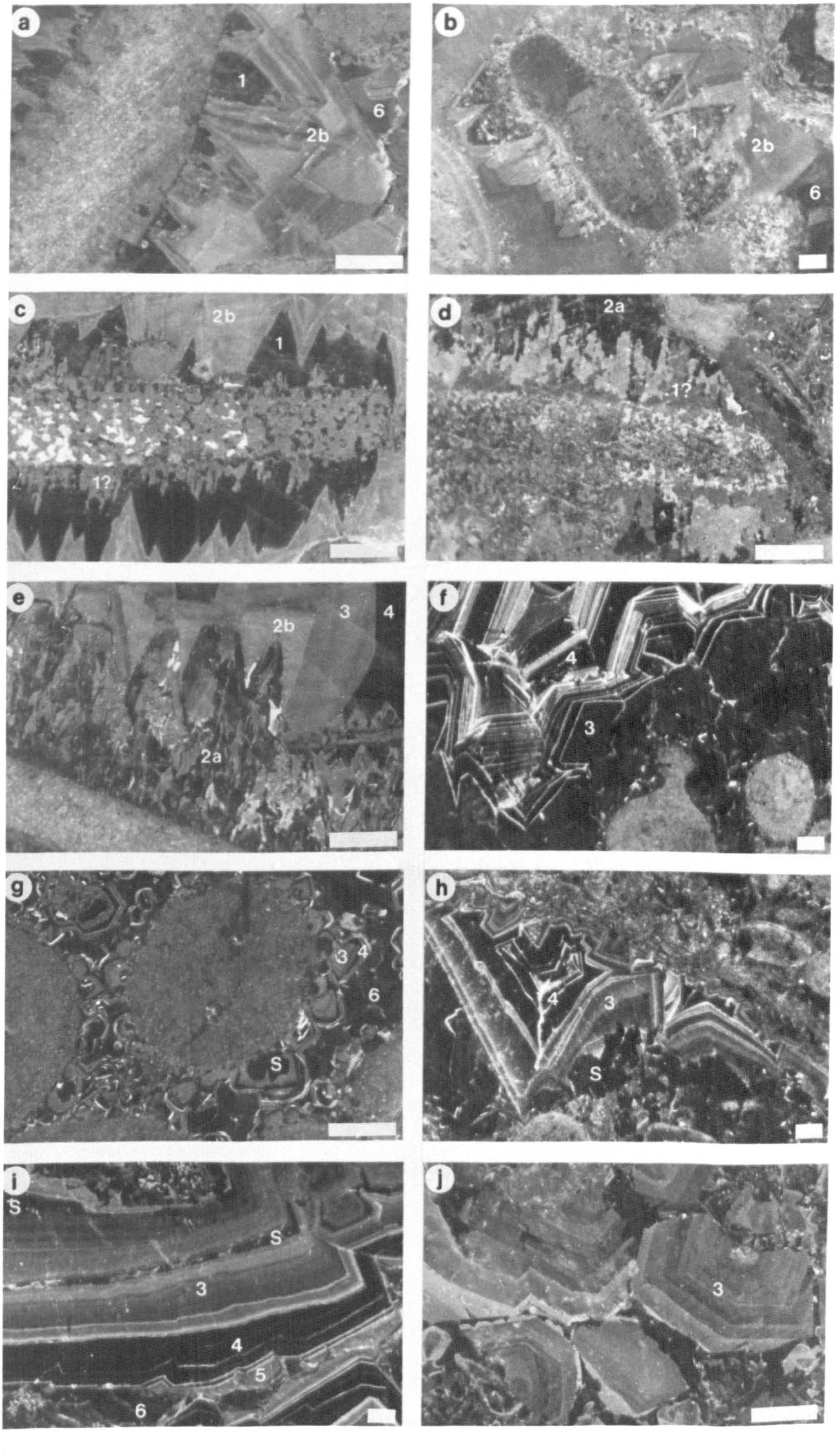
f)Sparry calcite containing ferroan Zone 3 which is dull luminescing.Sample 18337.

g)Sparry calcite containing dull luminescing Zone 3.Solution vugs (S) within Zone 3 are filled with non-luminescing calcite.Zone 3 is overlain by Zones 4 and 6.Sample 20586.

h)Zone 3 showing second order zonation pattern.Solution vugs (S) cut across the zonation pattern and are filled with non-luminescing calcite.Sample 17854.

i)Syntaxial overgrowth containing Zones 2a,3,4,5 and 6.Zone 3 shows second and third order zonation.Solution features (S) are identified.Sample 17882.

j)Possible Zone 3 cement from the Daren Ddu Beds.Sample 17886.


a
1
6
2b
b
1
2b
6
c
2b
1
1?
d
2a
1?
e
3
4
2b
2a
f
4
3
g
3
4
6
S
h
4
3
S
i
S
S
3
4
5
6
j
3

is uncertain. It may not be a primary precipitate. In future such areas are termed 'poorly defined Zone 1'. The origin of this is considered further in Chapter 3.

Zone 1 can be found occupying cavities that are presumed to have resulted from aragonite dissolution. There is no direct evidence as to the age of this zone, but indirect evidence suggests that it is 'early' since Zone 2b, an 'early' cement, commonly overlies it.

Zone 1 is illustrated in Fig. 2/13a-d.

Zone 2

This zone can be divided into two second order zones, a and b. Zone 2a is the inclusion-rich, non-ferroan calcite cement that typically occurs as syntaxial overgrowths and is described in 2.1 (Fig. 2/7g, h, 10c, d, 13d, e). Its 'early' age has already been postulated. Zone 2a cannot be considered as a true cement zone since it did not result from a single precipitation event. However, since the inclusion-rich calcite always occurs in the same position in the cement sequence it will be treated as such.

Zone 2b (Fig. 2/13a-c, e) consists of inclusion-free, non-ferroan calcite. It must be 'early' in age as it can be found lying between zones that have both been identified as 'early'. Its CL is dull to bright and, on occasions, shows second and third order zonation.

Zone 3

Zone 3 consists of inclusion-free calcite that is often faintly ferroan on staining, although, as mentioned in 2.1, it often appears non-ferroan in the Gilwern Oolite. Its CL is dull and usually shows second and third order zonation. Fig. 2/13 e-j illustrates some of the variability found in this zone.

Irregular areas filled with dominantly non-luminescing calcite are common within Zone 3. These are interpreted as solution features and are discussed in Chapter 3.

Evidence establishing the 'early' age of Zone 3 was furnished in 2.1.

Zone 4

Zone 4 is composed of inclusion-free, non-ferroan calcite. It is a combination of 'early' and 'late' cement. The difficulties involved in distinguishing the two were outlined in 2.2. Due to these difficulties both are included in the same first order zone. The CL has been described in 2.1 and 2.2.

The third order, brightly luminescing, hairline zones that are present in Zone 4 tend to be clustered to form a second order zonation pattern. This is highly variable, but it has been possible to distinguish four second order zones, a – d. Zone 4a is 'early' whereas Zones 4b, c and d are 'late'. It is not always possible to recognise the second order zones within Zone 4 calcite. This is particularly true of the Gilwern Oolite, especially the Coral Bed. Hairline, third order zones are virtually absent from the 'lozenge-shaped' crystals of the Gilwern Oolite although they are found in associated larger crystals that grow into moulds (Fig. 2/14i, j).

Zone 4 calcites are illustrated in Fig. 2/14. The third order zonation pattern is responsible for picking out changes in crystallographic form during growth. This is considered further in 2.4.

Zone 5

A dull to brightly luminescing zone commonly occurs at the outer edge of Zone 4 throughout most of the Oolite Group in the

Fig.2/14 ZONE 4 CEMENTS

a) Second order zonation within Zone 4 is defined by variations in the density of brightly luminescing, hairline, third order zones. Second order zones a, b and c and identified. Sample 17905.

b) Syntaxial overgrowth containing Zones 2a- 6. Zone 4 contains second order zones a and b. The latter lies unconformably on an etched surface (arrow) at the outer edge of a. Sample 18349.

c) Syntaxial overgrowth containing Zones 2a - 6. Zone 4 consists of second order zones b and c. Zone 4b lies unconformably on Zone 3 (arrow). Sample 18350.

d) Syntaxial overgrowth containing Zones 3 - 6. It is hard to decide which second order zones Zone 4 can be divided into. It probably represents Zone 4c. Sample 17882.

e) Syntaxial overgrowth containing Zones 2a - 5. Second order zones c and d are identified in Zone 4. Sample 17869.

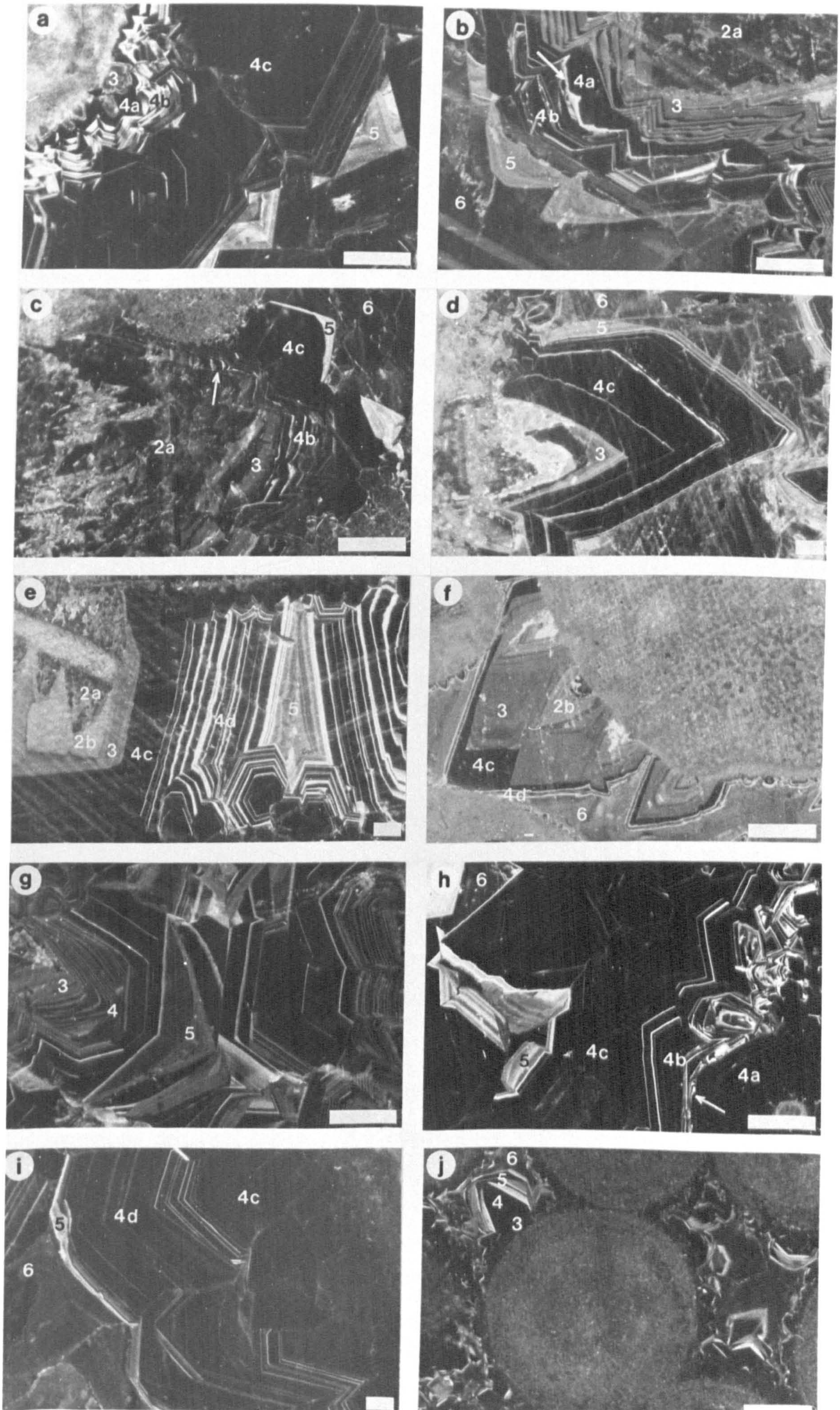
f) Syntaxial overgrowth containing Zones 2b, 3, 4 and 6. Zone 4 is thinner than is typical. It contains second order zones c and d. Sample 17836.

g) Sparry calcite containing Zones 3 - 5. Zone 4 cannot be divided into the second order zoned identified in the bulk of the Oolite Group. The brightly luminescing, hairline, third order zonation pattern highlights changes in crystallographic form that are typical of Zone 4 cements from the Coral Bed in the eastern portion of the outcrop. Sample 17825.

h) Sparry calcite containing Zones 4 - 6. The second order zonation is suggested. Zone 4b lies unconformably on Zone 4a (arrow). Note the changing crystallographic form in Zone 4b. Sample 20550.

i) Sparry calcite filling a mould in the Gilwern Oolite. Zones 4c and 4d are identified. Sample 20562.

j) Sparry cement crystals from the same sample as in (i). These crystals grew between ooids. Note the 'lozenge-like' shape and the lack of second order zonation within Zone 4. Sample 20562.



a
3
4a
4b
4c
5
b
2a
4a
3
4b
5
6
c
6
5
4c
2a
4b
3
d
6
5
4c
3
e
2a
2b
3
4c
4d
5
f
3
2b
4c
4d
6
g
3
4
5
h
6
5
4c
4b
4a
i
4c
5
4d
6
j
6
5
4
3

study area. This is Zone 5. It was identified as a 'late' cement in 2.2. Examples of Zone 5 are illustrated in Fig. 2/15a-f.

Zone 5 can often be identified as faintly ferroan by staining. However, it also occurs as a combination of ferroan and non-ferroan second order zones in which the ferroan calcite has a CL similar to that of the single ferroan zone described above, while the non-ferroan calcite is dominantly non-luminescing (Fig. 2/15e). At Coed Pant-y-daren the transition between one and more than one ferroan zone can be seen (Fig. 2/15d).

Despite the obvious variability of the zones labelled 5 in Fig. 2/15a-f, they are all thought to be equivalent since they lie in the same position in the cement sequence.

Zone 6

This zone is mainly composed of highly ferroan calcite that has a dull CL. It typically shows a patchy distribution of second order zones which do not correspond to a normal growth zonation pattern. Occasionally a more regular, although still not normal, growth zonation pattern is seen. This has been termed 'Fir-tree' zonation and its origins are considered in 2.4 Normal growth zonation is found within Zone 6 but this is largely restricted to later Zone 6 calcites. The later Zone 6 calcites show a progressive decrease in iron content and eventually become iron-free. The later non-ferroan Zone 6 is brightly luminescing. It is often found occupying fractures.

Some Zone 6 cements that show normal growth zonation seem unrelated to other Zone 6 cements. These have a second order

Fig.2/15 ZONE 5 AND 6 CEMENTS

a) Sparry cement crystals containing cement Zones 3 - 6. Zone 4 shows the typical 'lozenge-like' shape of the Gilwern Oolite. Zone 5 consists of a single, brightly luminescing zone. Zone 6 shows 'normal', although atypical, zonation. Sample 17856.

b) Sparry calcite crystals containing Zones 4 - 6. Zone 5 consists of two brightly luminescing second order zones separated by non-luminescing calcite. Zone 6 shows zonation similar to that seen in (a). Sample 20594.

c) Sparry calcite containing Zones 4 - 6. Zone 5 consists of a single, brightly luminescing zone. Sample 17906.

d) Cement crystal in which Zone 5 contains two ferroan, brightly luminescing second order zones. These are separated by an intermittent layer of non-luminescing calcite (arrow). Sample 20558.

e) Sparry calcite containing Zones 4 and 5. Zone 5 contains at least three ferroan, dull luminescing, second order zones separated by dominantly non-luminescing calcite. Sample 18339.

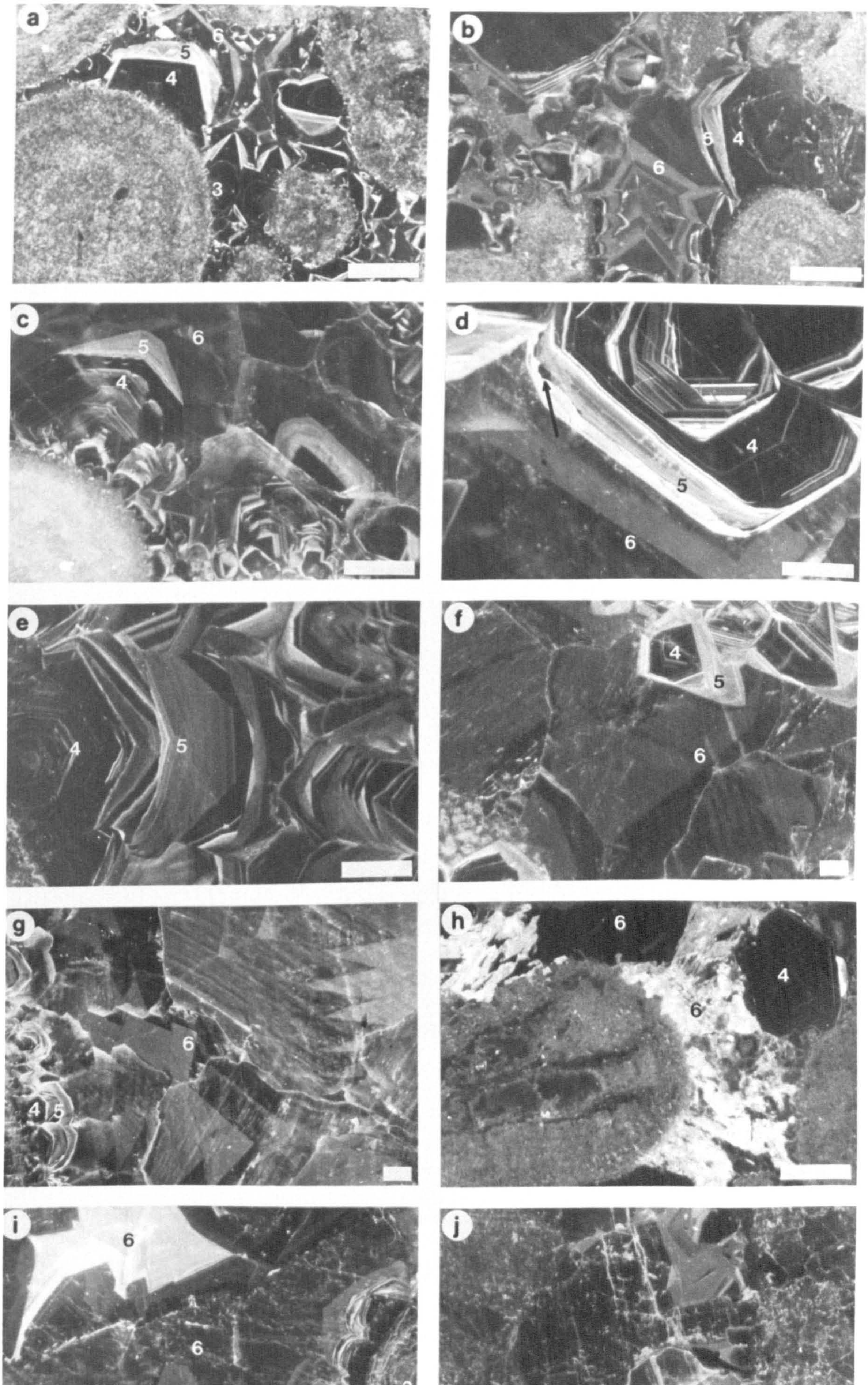
f) Sparry calcite showing Zones 4 - 6. Zone 6 shows typical patchy zonation. Sample 17887.

g) Some Zone 6 shows regular, 'Fir-tree' zonation. Sample 17862.

h) Sheafs of brightly luminescing calcite within Zone 6. Sample 20552.

i) Initial Zone 6 calcite is strongly ferroan and has dull luminescence. Late Zone 6 calcite is non-ferroan and brightly luminescing. Sample 21661.

j) Zone 6 from a vein. Brightly luminescing calcite fills later fractures. Sample 17869.


a
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4
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c
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6
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d
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5
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e
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5
f
4
5
6
g
6
4
5
h
6
4
6
i
6
6
3
5
4
j

zonation pattern of ferroan-non-ferroan-ferroan calcite. The intermediate calcite is brightly luminescing, but is often absent from the sequence (Fig. 2/15a, b).

In some instances Zone 6 consists of a patchy distribution of calcite and ferroan calcite . The distribution of the calcite, which is brighly luminescing, can be irregular, in sheafs (Fig. 2/15h) or in elongate areas parallel to twin lamellae. The latter is illustrated and discussed in 2.5.

Cements of Zone 6 are illustrated in Fig. 2/15f-j.

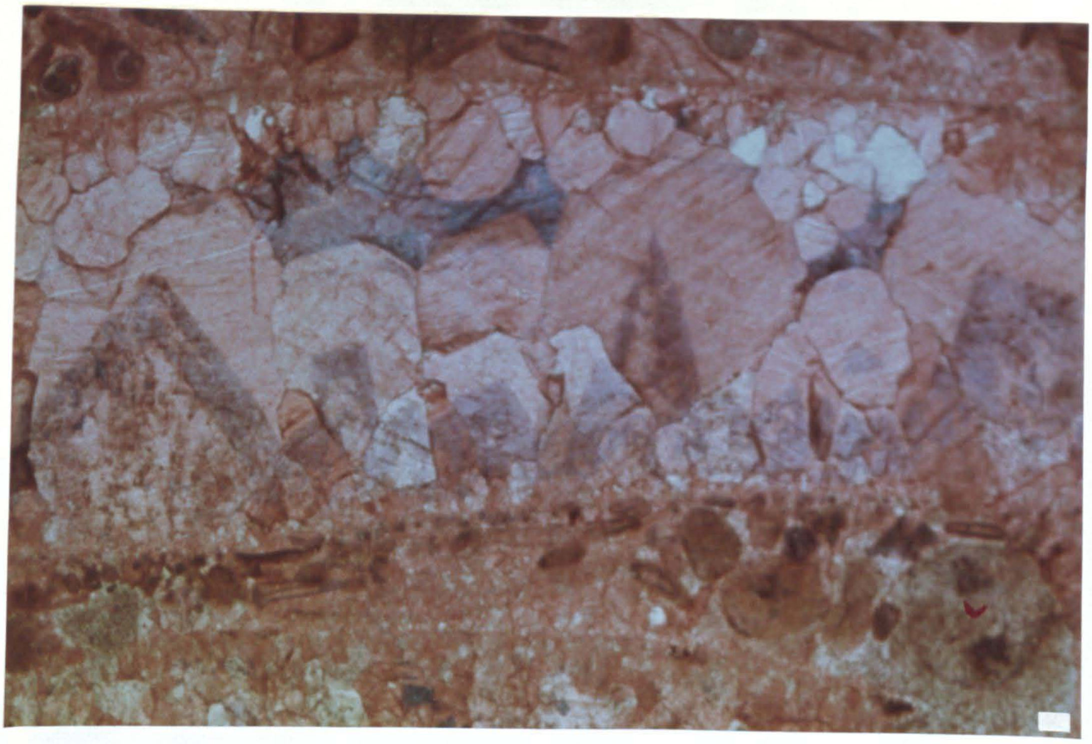
Zone 7

The final cement zone is ferroan dolomite showing undulose extinction and curved clevage. It occurs both as a pore filling and as a replacement mineral. This type of dolomite has been called saddle dolomite by Radke & Mathis (1980) and baroque dolomite by Folk & Asserreto (1974). It is non-luminescing.

The cements found throughout most of the Oolite Group consist of Zones 2a, 3, 4, 5 and 6 (Plate 2/2a). Zones 1 and 2b are restricted to the Pwll-y-cwm and Blaen Onneu Oolites in the Clydach area (Plate 2/2b). Some cements do not fit into this pattern at all well. These include some of the 'early' cements described in 2.1 and many of the cements from the Daren Odu Beds. For instance in the cements from sample 17879 (Plate 2 /3) the following zones can be identified:

1. inclusion-rich syntaxial overgrowths which are dominantly ferroan but are zoned with non-ferroan calcite;
2. ferroan calcite;
3. non-ferroan calcite (this is very rare); and
4. patchily zoned ferroan calcite, probably equivalent to Zone 6.

a



b

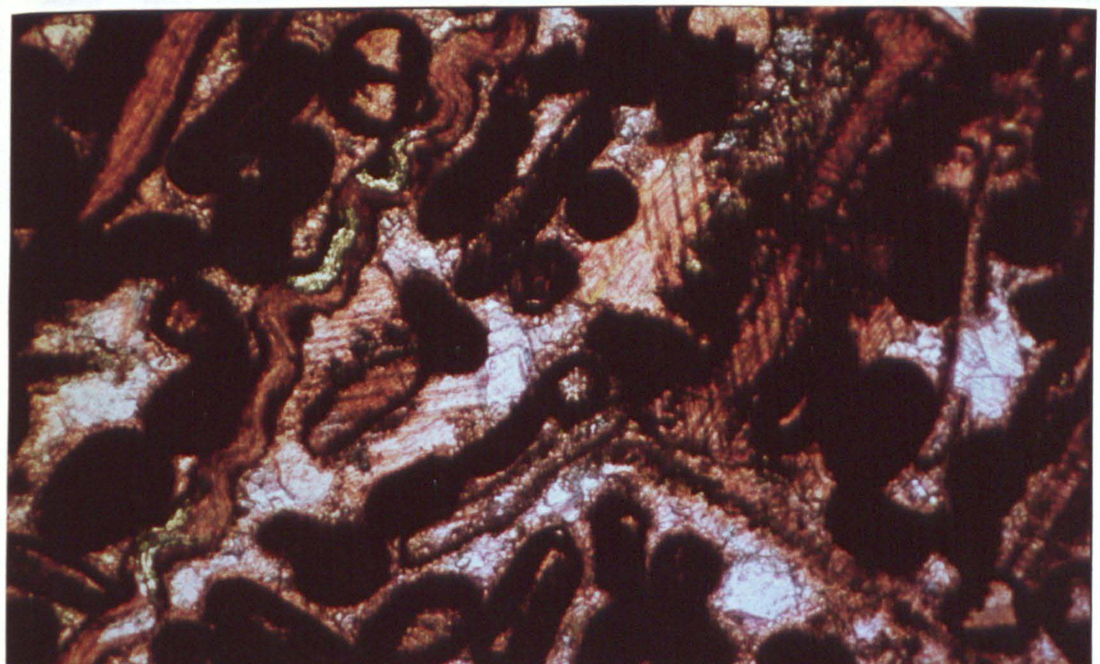


Plate 2/2 CEMENT CRYSTALS SHOWING THE TYPICAL ZONATION PATTERN

a) Transmitted light photomicrograph of a stained thin section. Calcite cement crystals growing into a bivalve(?) mould contain Zones 2a, 3, 4, 5 and 6. Sample 18303.

b) Transmitted light photomicrograph of a stained thin section. Calcite cement contains Zones 1, 2b and 6.

Plate 2/3 CEMENT CRYSTALS SHOWING ATYPICAL ZONATION

Transmitted light photomicrograph of a stained thin section.The zonation seen in this sample cannot be correlated with the typical zonation scheme.Sample 17879.

Difficulties involved with correlating cement zones

It is obvious from the illustrations of the cement zones already given in this section that there is much variation within a given zone and it may be difficult to correlate on anything other than a first order zone level from one sample to another. Over what distance can a detailed correlation on a second order zonal level or more be made? The difficulties of correlating over ever increasing distances is discussed below. Reasons are suggested to explain the difficulties encountered.

Correlation within a single crystal:

The zonal pattern seen in thin section through each crystal is usually constant. However, there are three situations where this is not true:

1. discontinuity surfaces within crystals.

   In some crystals it has been noted that zones stop part of the way around the crystals (Fig. 2/16a). The incomplete zones may represent the recommencement of precipitation after a hiatus in growth. Each successive layer of calcite precipitated is deposited in lattice continuity on the crystal below. After a pause in growth the next layer precipitated may be incomplete perhaps reflecing some contamination of surface during the period of no growth;

2. changing crystal form.

   Many of the cements of the Oolite Group display constantly changing crystal form (see 2.4). Crystal form is changed by the preferential growth of certain faces. Changing form will result in a variation in the zonal pattern through the crystal. In sections cut obliquely to the c-axis this may result in a variation in the zonal pattern around the crystal

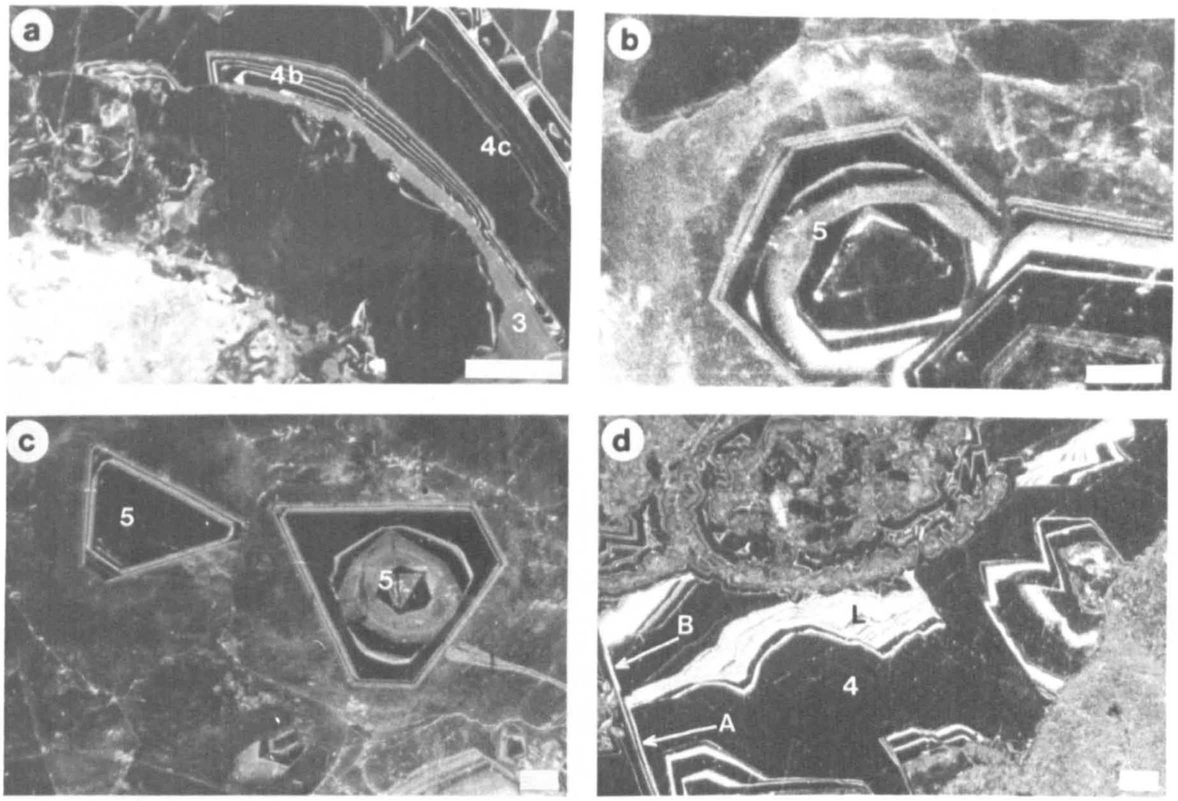
Fig.2/16 VARIATIONS IN ZONATION PATTERNS WITHIN AND BETWEEN CRYSTALS

a)Discontinuous zones around a crystal.The initial calcite precipitated on top of Zone 3 only covers part of the surface.Sample 17878.

b)Section through a crystal cut approx. perpendicular to the c-axis.The zonation pattern varies around the crystal.Sample 18303.

c)Two sections through crystals both cut approx. perpendicular to the c-axis. The zonation seen varies with the level at which the section is taken. Sample 18303.

d)Syntaxial overgrowth containing hairline,third order zones A and B.A and B expand to give brightly luminescing bands (L) on the faster growing faces. Sample 17905.



a
4b
4c
3
b
5
c
5
5
d
B
L
A
4

(Fig. 2/16b). This is particularly true of sections cut through the terminations of crystals. Also sections taken at different levels through the crystal will reveal different zonations (Fig. 2/16c). This is also the case for simple crystals which have a constant form. The most complete zonal sequences are usually seen in sections cut parallel to the c-axis through the centre of the crystal.

3. variations in growth rate around a crystal.

Crystals may grow more rapidly in one direction than another (syntaxial overgrowths on echinoderms are a common example). A zone will be thicker on the face that is growing faster. Fig. 2/16d illustrates such a case. Hairline zones A and B are not recognisable on the faster growing face but are equivalent to brightly luminescing zoned bands, A is equivalent to L. If such variations in growth rate were represented by crystals growing in separate pores the two cement sequences would be difficult or impossible to correlate although they are equivalent. Usually, however, the case is not this extreme.

Correlation between 'nearby' pores and/or moulds

'Nearby' in this context is taken to mean in the same thin section. All crystals within a pore tend to have a similar zonal pattern although cut effects, the other factors discussed above and a variety of substrates can cause some variation. Although it is apparent that the cement zones identified in the Oolite Group can be correlated over many kilometres, the correlation between nearby pores can often be made on only the crudest of levels. This is illustrated below by a number of examples.

SAMPLE 17882, Blaen Onneu Oolite, Darren

The thin section studied is illustrated in Fig. 2/17. It contains three shelter cavities below brachiopod valves in a pelsparite. As can be seen there is a marked variation in the proportion of Zones 3-6 in these areas. The increased thickness of Zone 3 in the lowest cavity implies an increased growth rate which has resulted in a much more detailed second and third order zonation being visible. The variation in thickness is not related to cavity size since they have similar dimensions. The condensed sequence in the upper cavities cannot be recognised in the expanded sequence of the lowest cavity.

SAMPLE 18303, Coral Bed, Twyn-y-dinas

This sample contains many bivalve moulds. They are illustrated in Fig. 2/18. Zones 2-6 can be identified by staining and the distribution of these zones are summarised in Fig. 2/19. It is clear that:

1. most moulds contain Zone 2a, so dissolution of the bivalves must have occurred prior to Zone 2a precipitation;
2. the majority of moulds contain Zone 4;
3. the complete cement sequence is not seen in any of the moulds;
4. Zones 3, 5 and 6 are rare and often absent.

These initial observations suggest that the filling of the moulds was not a simple process. Precipitation occurred in different moulds at different times and at different rates.

Fig.2/17 VARIATION IN CEMENT ZONATION IN A THIN SECTION

A sketch of a thin section from Sample 17882 shows brachiopod valves(black), pelsparite(stippled) and shelter cavities filled with calcite spar(white). CL photographs of the cements from each of the shelter cavities show varying thickness and proportion of the various cement zones present. Scale bar of photomicrographs represents 200μm.

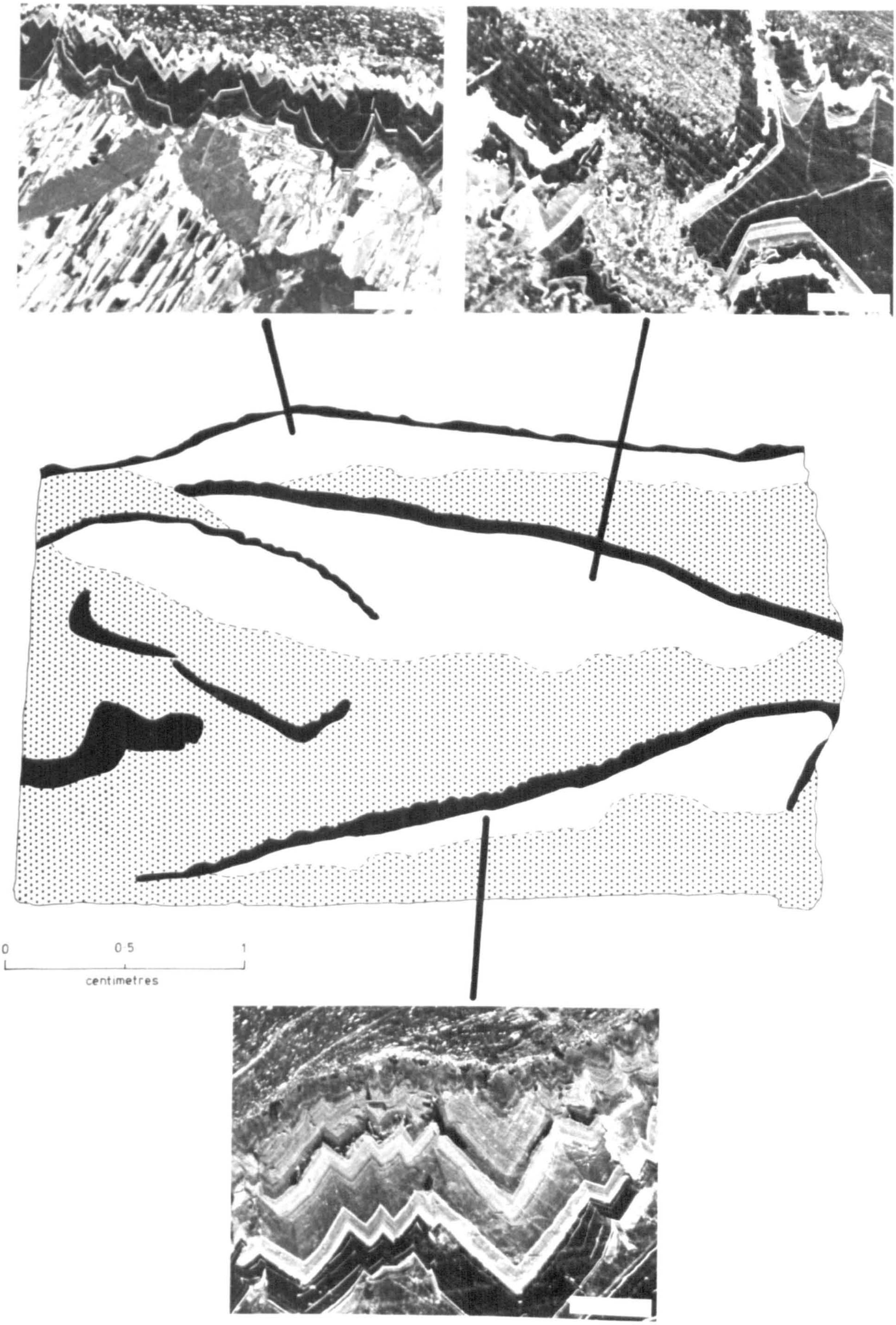
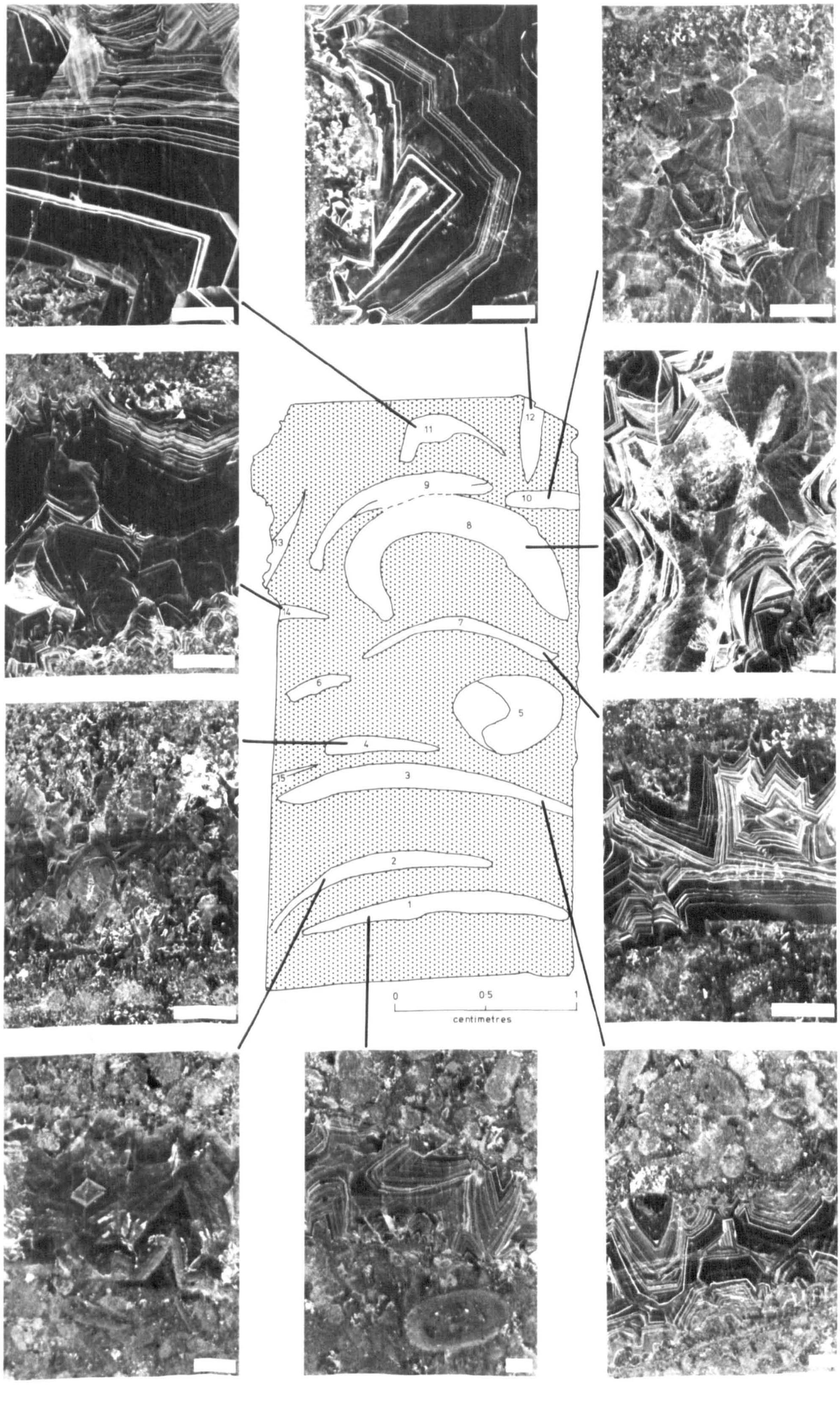

0
0·5
1
centimetres

Fig.2/18 VARIATION IN CEMENT ZONATION IN A THIN SECTION

A sketch of a thin section from Sample 13303 shows pelsparite(stippled) and spar filled moulds(white).CL photographs of cements from ten of the moulds show that there is much variation in the zonal pattern over small distances. Scale bar of photomicrographs represents 200μm.


11
12
9
10
8
13
14
7
6
5
4
15
3
2
1
0
0·5
1
centimetres

	MOULD														
ZONE	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
2	○	○	—	—	○	○	○	—	—	○?	○	○	—	○	○
	●	●	●	●?	●?	●	●	●	●	●?	●	●	●	●	●
3	○	○	—	—	○	—	—	—	—	—	—	—	—	—	—
	—	●	—	●	●	●	●	—	●	●	●	—	—	●	●
4	○	—	○	○	—	○	○	○	○	○	○	○	○	○	—
	—	—	●?	●	—	●	●	●	●	—	●	●	●	●	●
5	—	—	—	—	—	—	—	○	○	—	—	—	—	—	—
	—	—	●	—	—	—	—	●	●	—	—	—	●	—	—
6	—	—	○	—	—	—	—	○	○	—	—	—	—	—	—
	—	—	●	—	—	—	—	●	●	—	—	—	—	—	—

● very rare
●
● ↓
● abundant

Fig.2/19 THE DISTRIBUTION OF ZONES 2a-6 IN THE AREA ILLUSTRATED IN Fig.2/18

Table showing the distribution of cement Zones 2a - 6 within the moulds illustrated in Fig.2/18. (o - zone can be identified by staining; ● - zone can be identified by CL)

When the CL of the cements is also considered the situation becomes even more complicated. The CL of the cement filling 10 of the moulds is snown in Fig. 2/18. The major observations that can be made from this new information are:

1. cements that have been assigned to Zone 4 have greatly varying CL second and third order zonation patterns. Occasionally cements from adjacent mould may show similarities.
2. the typical zonation pattern that is pervasive throughout the eastern section of the Coral Bed and is dominated by Zones 4-6 is only present in mould 8/9, earlier zones being very thin;
3. Zone 3 has been identified in moulds using CL where it was not apparent with staining (Fig. 2/19). In these situations it is very thin;
4. mould 1 has a cement whose CL is unlike that of any other in the Coral Bed (or elsewhere). The ferroan zone that might have been identified as Zone 3 by staining, in fact is not Zone 3.

CL confirms that the filling of the moulds was a heterogeneous process. The variation in the zonal patterns can be explained by the following processes:

1. filling of the moulds did not occur at the same time. While precipitationwas occurring in one mould it was not necessarily occurring in another nearby. The variations in the location of precipitation at a given time may be controlled by a number of factors:

a. substrate - this may have an inhibiting (as in the case of contaminated surfaces) or an enhancing (as in the case of large seed crystals) effect;

b. permeability of the surrounding material - inherent variation in the permeability will control the path taken by pore fluids passing through the rock. This may result in small volumes being periodically isolated from the ambient pore fluids;

2. variations in growth rate both within and between crystals. The causes of this are likely to be the same as discussed in 1a, b above.

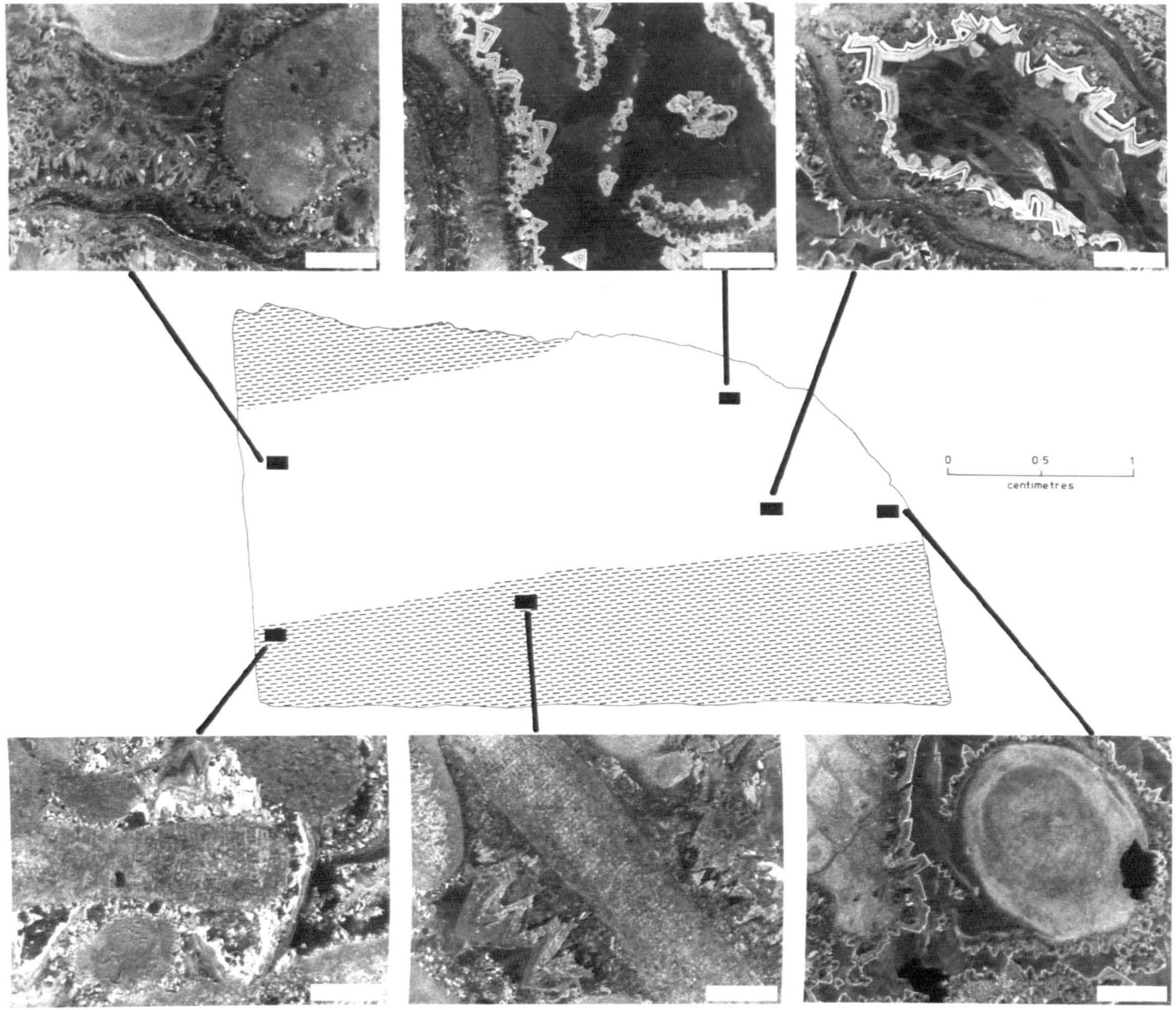
3. variations in the chemistry of microenvironments. Although the gross chemistry of the precipitating fluids is governed by factors outside the study area, small variations may occur as the result of local effects. Changes in Eh would be particularly important since this would affect the Mn and Fe content of the calcite precipitated and hence the CL (Oglesby, 1976). If such variations were on the scale of a single mould it would explain some of the variations of the zonation pattern in given zones. Small scale variations in chemistry may also explain the development of 'atypical' zonations as seen in Mould 1. Such changes may be influenced by the isolated occurrence of decaying organic matter or exotic sources of Mn^{2+} and Fe^{2+} ions.

SAMPLE 17829, Pwll-y-cwm Oolite, Daren Ddu

The variation within a section from this sample is illustrated in Fig. 2/20. There are six distinct areas within 2 cm^2!

Fig.2/20 VARIATION IN CEMENT ZONATION IN A THIN SECTION

A sketch of a thin section from Sample 17829 distinguishes areas that have undergone compaction and pressure solution(dashed)from those that have not (white).CL photographs show the variation that is found within the cement. Scale bar of photomicrographs represents 200µm.


0
0·5
1
centimetres

The following observations can be made:

1. late cements are restricted to areas that retain high porosity, i.e. that have not undergone pressure solution;
2. pre-Zone 6 cements are best developed within the largest pores, especially within brachiopod shells;
3. the earliest zones are only present as syntaxial overgrowths and are largest on the largest seed crystals;
4. possible solution features have a very limited distribution. They are found in the areas that have undergone pressure solution.

As in previous examples cementation has been a heterogeneous process. Pressure solution and compaction seem to control the distribution of Zone 4 and 5 cement, it being excluded from areas in which this has occurred. Pressure solution and compaction will cause a decrease in permeability and hence pore fluids will move less easily through areas in which this has occurred. The presence of thicker cement zones within shell cavities may also be a permeability effect, the shell cavities being large voids within the rock.

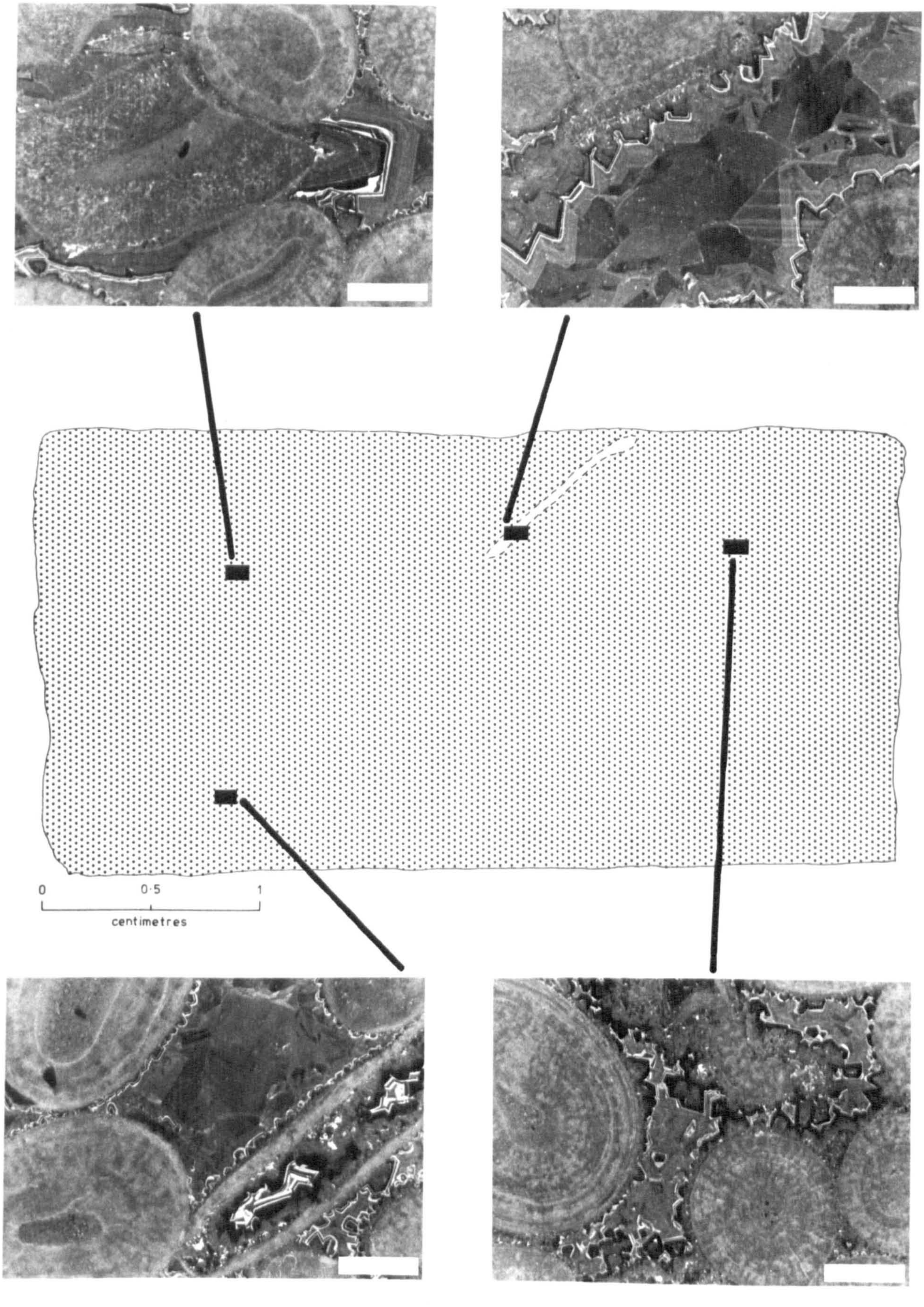
The effect of substrate on the zonal pattern developed is illustrated by the earliest cement being observable only as syntaxial overgrowths. Thus the zonal pattern seen in a rock is also a reflection of the allochems that make up that rock.

SAMPLE 18335, Pwll-y-cwm Oolite, Daren Ddu

Variations in the relative abundance of zones even occurs in the most homogeneous of rocks. Fig. 2/21 shows cements from a pure, well sorted oosparite. Again substrate plays

Fig.2/21 VARIATION IN CEMENT ZONATION IN A THIN SECTION

A sketch of a thin section from Sample 18335 shows oosparite(stippled) and spar filled moulds(white).CL photographs show variations in the proportion of cement zones at different places within the thin section.Scale bar of photomicrographs represents 200µm.


0
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a role in controlling the relative thickness of zones, early zones predominating in syntaxial overgrowths on rare echinoderm fragments. The variation in thickness and relative abundance of zones probably mainly reflects small, inherent variations in the permeability of the sediment, despite its homogeneity.

Correlation between samples

In the light of the foregoing discussion it seems incredible that it is possible to correlate zones between samples that are kilometres apart, with any confidence. However, this is possible and in some cases correlation can be very detailed. That this can be done is mainly due to the following facts:

1. many of the problems encountered with correlation on a thin section scale are a direct result of the inherent inhomogeneity of the rock, i.e. variations in allochems, pore size, etc. By taking a large enough sample many of these problems are overcome. Nevertheless, it is often necessary to piece together the complete cement sequence;
2. the chemical variations causing the zonal sequence seen are of external origin. Local effects are too minor to significantly affect this. However, it may be sufficient to affect the second and third order zonation. If such changes occur on a centimetre scale it would be impossible to correlate between samples on anything more than a first order level.

The distribution of the cement zones within the study area

The distributions of the cement zones outlined earlier in this section are illustrated in Fig. 2/22-25, and are described below:

Zone 1

The distribution of Zone 1 cements is shown on Fig. 2/22a. They are restricted to the Blaen Onneu and Pwll-y-cwm Oolites in the Clydach area. The dolomitisation that affects these oolites to the east of the Clydach area means that it is impossible to trace Zone 1 cements further eastwards. 'Poorly defined' Zone 1 cements have a wider distribution but, due to their uncertain origin, the significance of this distribution is unclear.

Zone 2

Zone 2a has a wide distribution (Fig. 2/22b). Zones 1 and 2a are mutually exclusive. This makes it impossible to assess the relative ages of these zones, but it is possible that they are laterally equivalent. The abundance of Zone 2a has been evaluated on a purely qualitative basis. It is most abundant in bioclastic samples. This is because these have larger pore spaces and they contain a higher proportion of allochems on which syntaxial overgrowths can develop. Sampling bias has probably resulted in the overestimation of the amount of Zone 2a in rocks which contain bioclastic laminae since these areas were examined preferentially. The absence of this zone from the Clydach Beds may well reflect the lack of suitable substrate in these beds on which syntaxial overgrowths could grow and the fine grained nature of these rocks.

The presence of abundant brightly luminescing calcite within Zone 2a (discussed in Chapter 3) is restricted to several horizons, the most prominent and widespread occurring at the base of the Coral Bed. Its abundance is not associated with the abundance of the zone itself. Another horizon occurs within the Blaen Onneu Oolite in the western portion of the outcrop.

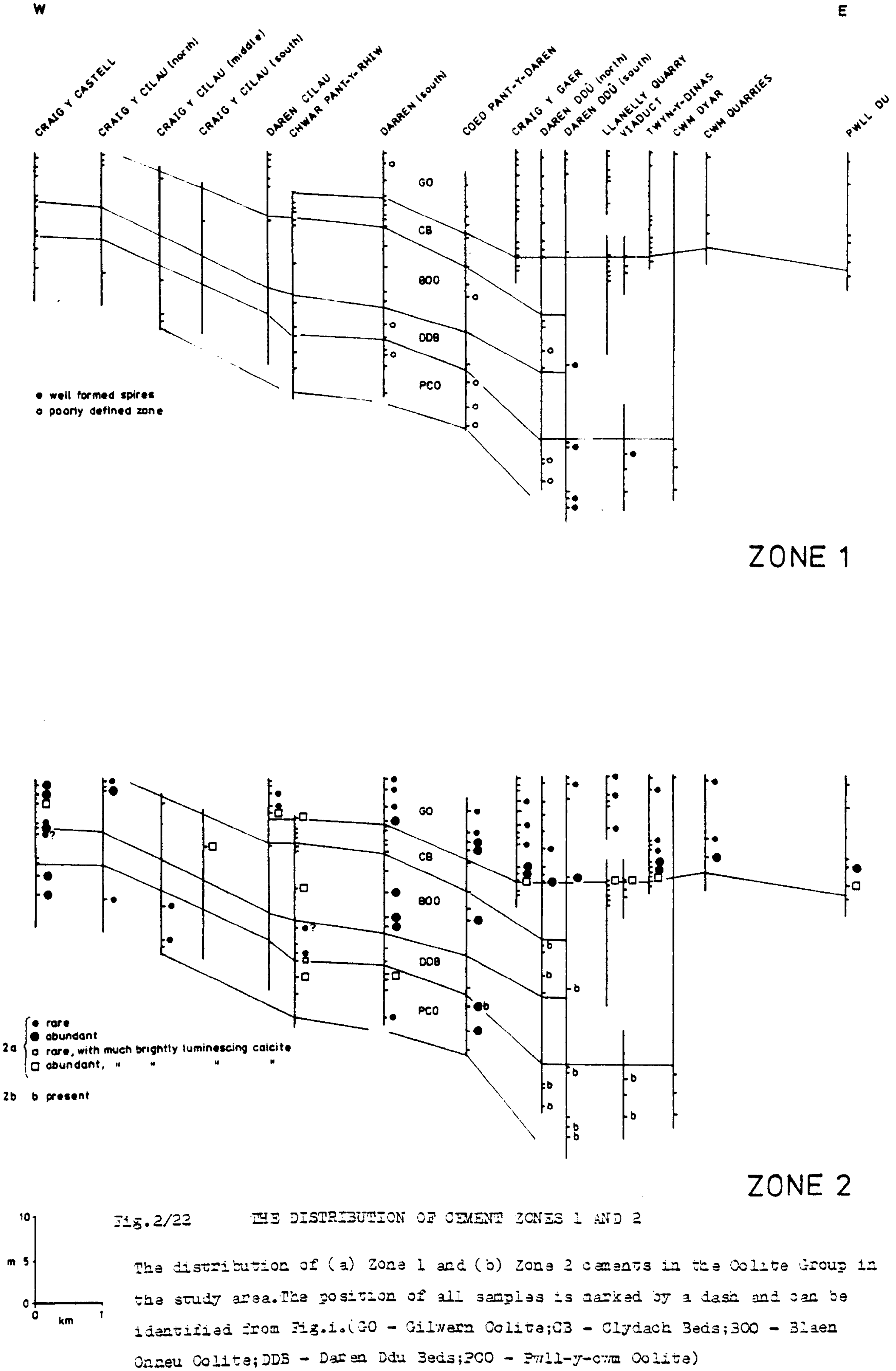


Fig.2/22 THE DISTRIBUTION OF CEMENT ZONES 1 AND 2

The distribution of (a) Zone 1 and (b) Zone 2 cements in the Oolite Group in the study area. The position of all samples is marked by a dash and can be identified from Fig.i.(GO - Gilwern Oolite; CB - Clydach Beds; BOO - Blaen Onneu Oolite; DDB - Daren Ddu Beds; PCO - Pwll-y-cwm Oolite)

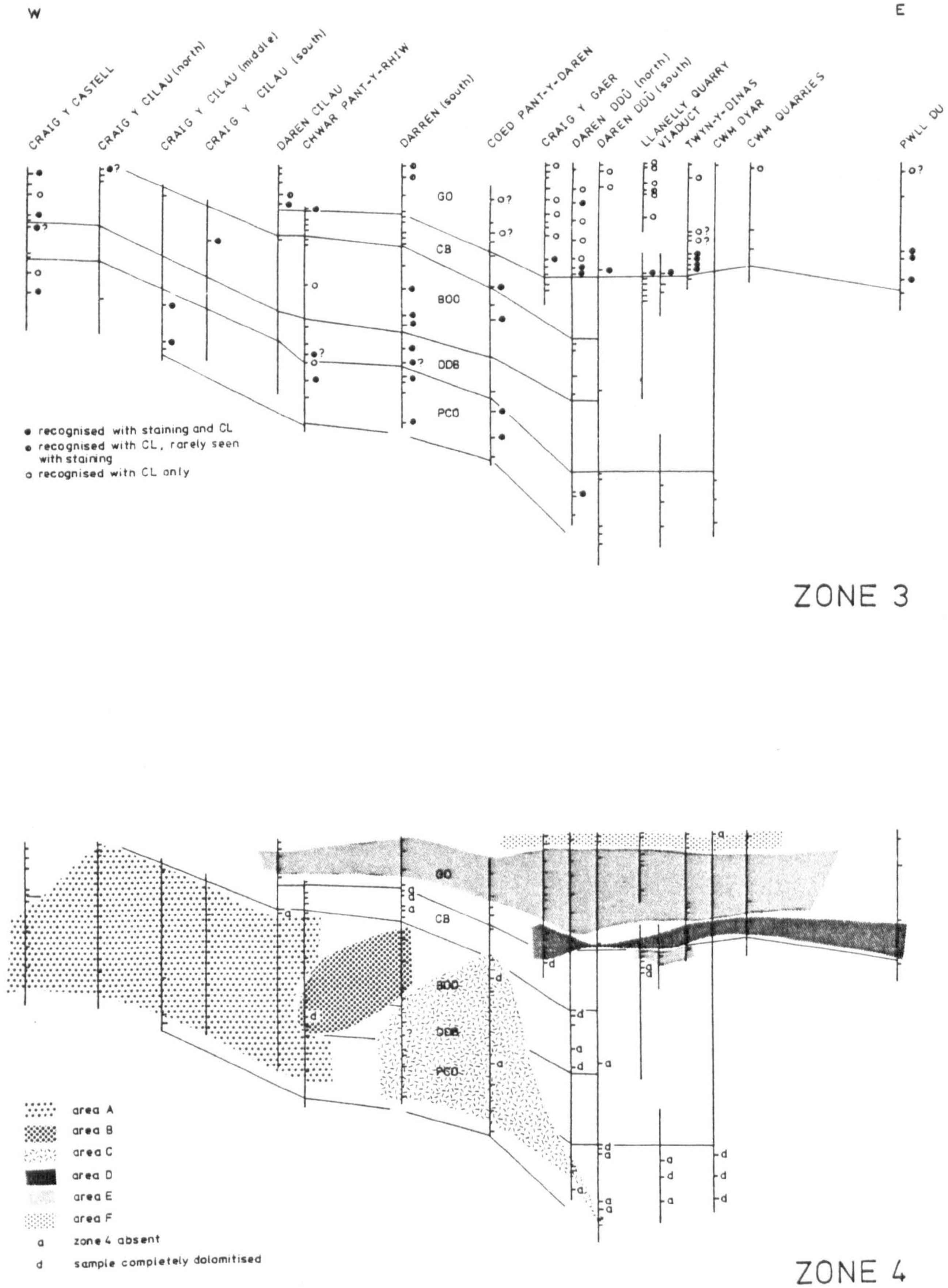
Zone 2b has a similar distribution to Zone 1, being restricted to the Blaen Onneu and Pwll-y-cwm Oolites in the Clydach area. However, it does extend as far west as Coed Pant-y-daren where it lies between Zones 2a and 3 (Fig. 2/13e).

Zone 3

In Fig. 2/23a a distinction is made between Zone 3 cements that can be recognised as ferroan by staining and those which cannot. Non-ferroan Zone 3 is restricted, almost entirely, to the Gilwern Oolite above the Coral Bed. Isolated examples of ferroan Zone 3 are found within the Gilwern Oolite and occasionally non-ferroan Zone 3 is found elsewhere. It was pointed out in 2.1 that the non-ferroan nature of some of the Zone 3 calcite may be an artifact and not a reflection of the true situation. If Zone 3 within the Gilwern Oolite is truly non-ferroan, then the change to ferroan calcite with increasing depth must reflect a change in either the environment of precipitation or the chemistry of the parent fluids of Zone 3. The lack of non-ferroan Zone 3 at the top of the Oolite Group in the west of the outcrop is associated with the disappearance of the Gilwern Oolite, to which the non-ferroan Zone 3 calcite is restricted. This is in accordance with its identification as 'early'.

As with Zone 2a, Zone 3 is absent from the Clydach Beds, probably for the same reasons as for Zone 2a.

In the Clydach area Zone 3 is found within the Gilwern Oolite. However, in the Blaen Onneu and Pwll-y-cwm Oolites it thins and disappears eastwards from Coed Pant-y-daren. In these oolites its most easterly extent is Daren Ddu. Here it is found overlying Zone 2b (Fig. 2/14f). This distribution is similar to that of Zone 2a.



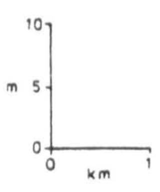


Fig.2/25 THE DISTRIBUTION OF CEMENT ZONES 3 AND 4

The distribution of (a) Zone 3 and (b) Zone 4 cements in the Oolite Group in the study area.The position of all samples is marked by a dash and can be identified from Fig.i.(GO - Gilwern Oolite;CB - Clydach Beds;BOO - Blaen Onneu Oolite;DDB - Daren Ddu Beds;PCO - Pwll-y-cwm Oolite)

Zone 4

As with Zones 2a and 3, Zone 4 thins and disappears eastwards from Coed Pant-y-daren within the Blaen Onneu and Pwll-y-cwm Oolites. In these oolites its easterly limit is Daren Ddu. Other than this Zone 4 is rarely absent. An attempt has been made to group samples into areas showing similar second order zonation patterns. These are represented by the variously shaded areas on Fig. 2/23b. These areas are considered in turn below.

Area A: Here Zone 4 consists of second order zones a, b and c (Fig. 2/14a). Often a marked 'unconformity' exists between a and b (Fig. 2/14b, c). The greatest similarity between samples in this area is shown by the Pwll-y-cwm Oolite. The variability within the rocks in the overlying portion of the section is such that often Zone 4 cannot be considered similar enough to be included into this area. The cause of such variability has already been considered.

Area B: In this area Zone 4 cements are simple, containing few brightly luminescing, hairline third order zones. These are probably Zone 4c calcites (Fig. 2/14d).

Area C: Zone 4 calcites in this area are transitional with those found in Areas A and B. They contain Zones 4c and 4d (Fig. 2/14e). Occasionally, Zone 4b is present, lying unconformably on Zone 3, confirming this interpretation. Further eastwards in Area C, Zone 4 becomes thinner. This is accompanied by a decrease in the number of third order zones present in 4d. At the eastern limit only two such zones are present (Fig. 2/14f).

Area D: This area is restricted to the Coral Bed in the eastern portion of the outcrop. It is difficult to place the second order zones seen in this area within the second order zonation scheme developed for Areas A-C (Fig. 2/14g).

As one moves westwards the cements of Area D cease to show their typical zonation and changes in crystallographic form. This is largely achieved between Craig y Gaer and Coed Pant-y-daren. Cements from the Coral Bed at Coed Pant-y-daren show similarities within Zone 4 cements from lower in the same section. The outer portion can be identified as Zones 4c and 4d. The nature of the inner portion is unclear.

Area E: In this area Zone 4 consists of 'lozenge-shaped' crystals containing few third order zones (Fig. 2/14j). The cements of this area are related to those found in Area D in that the crystals have similar terminations and to Area C in that larger crystals found filling moulds contain Zones 4c and 4d (Fig. 2/14i).

Area F: This area has the same spacial distribution as the pure oosparite at the top of the Gilwern Oolite. The cement cannot be correlated with that in any other of the areas. Since this cement has been identified as 'early' (see 2.1) whereas most of Zone 4 in Areas A-E is 'late' this is not surprising. Within the area itself the cements are variable. Specific zonation patterns can only be correlated over a few hundred metres at the most.

Zone 5

As with Zone 3, it is possible to divide Zone 5 cements into two types on the basis of whether they can be identified as ferroan by staining. A distribution very similar to that of Zone 3 exists

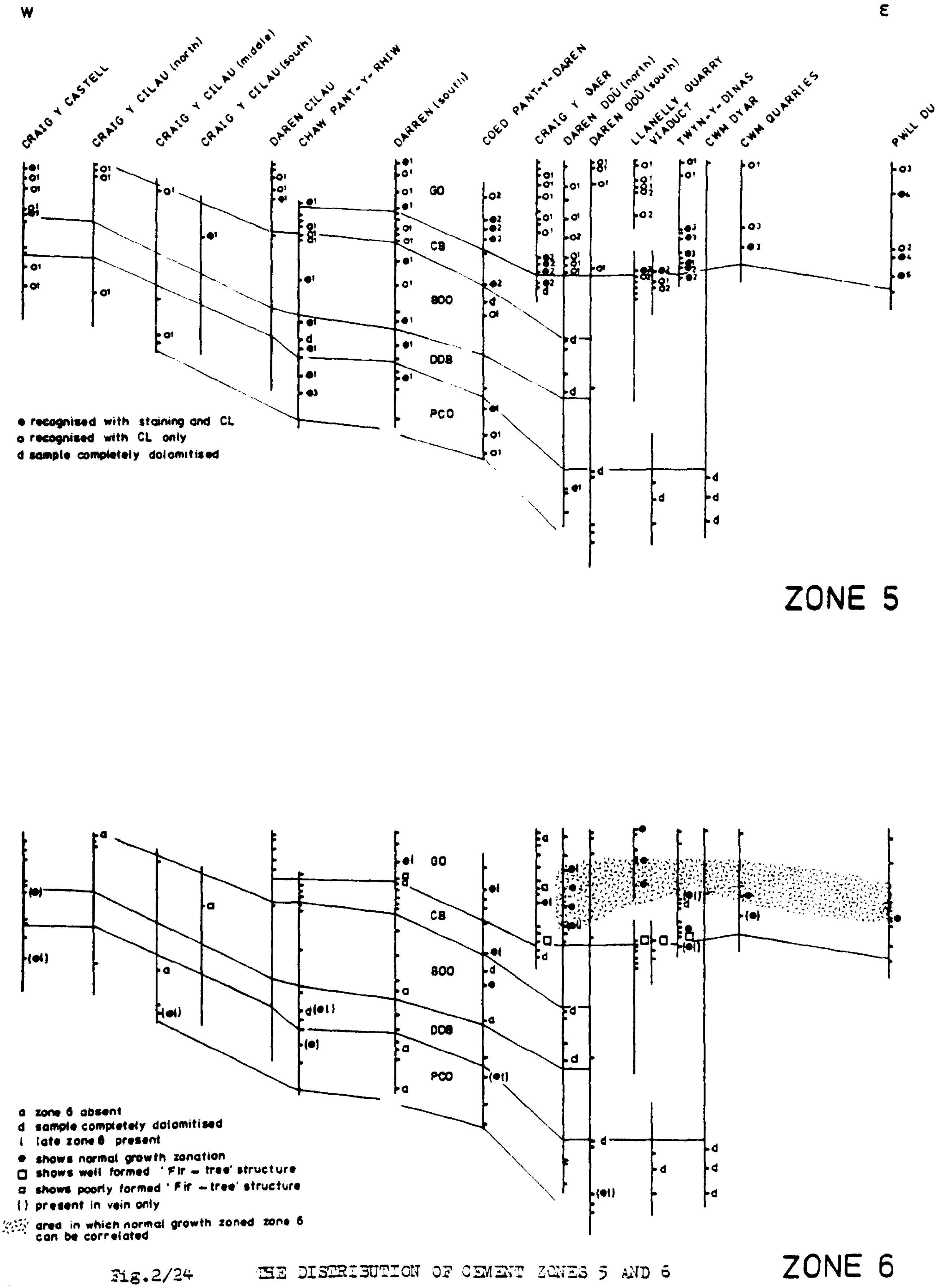


Fig.2/24 THE DISTRIBUTION OF CEMENT ZONES 5 AND 6

The distribution of (a) Zone 5 and (b) Zone 6 cements in the Oolite Group in the study area. The position of all samples is marked by a dash and can be identified from Fig.1. (GO - Gilwern Oolite; CB - Clydach Beds; BOO - Blaen Onneu Oolite; DDB - Daren Ddu Beds; PCO - Pwll-y-cwm Oolite) for ferroan and non-ferroan Zone 5, although there appears to be more cases of non-ferroan Zone 5 within the Blaen Onneu and Pwll-y-cwm Oolites (Fig. 2/24a). As with Zone 3 this division may result from the inadequacy of staining technique rather than a reflection of the true situation. This is thought to be more likely in this case because:

1. Zone 5 only stains very faintly and is often hard to identify even in large crystals;
2. Zone 5 is often present on only a few crystals and is usually very thin when it does occur. Due to the difficulty in identifying it, it is easy to miss occurrences of it when examining stained thin sections;
3. the precipitation of Zone 5 occurred after erosion of the Gilwern Oolite. Therefore on would not expect that the junction between ferroan and non-ferroan Zone 5 would occur parallel to the bedding, a fact that would suggest that precipitation happened prior to the erosion of the Gilwern Oolite.

More work needs to be done to clarify the situation.

Zone 5 has a similar distribution to Zones 2a, 3 and 4 in the Blaen Onneu and Pwll-y-cwm Oolites in the Clydach area. Like Zone 4 it does occur within the Clydach and Daren Odu Beds of that area.

The tendancy for Zone 5 to develop alternating ferroan and non-ferroan second order zones in an eastward direction is shown in Fig. 2/24a (see numbers indicating the number of brightly luminescing second order zones present). Laterally, the development of second order zonation occurs between Darren and Coed Pant-y-daren. In the eastern half of the outcrop, except at Pwll du, there is also a vertical decrease in the number of second order zones present, most of the Zone 5 occurring within the Gilwern Oolite consisting of a single, undivided zone. It is interesting to note that the disappearance of second order zonation in Zone 5 coincides with the western limit of Area D of Zone 4. It is not clear whether this is by chance or not.

Zone 6

Zone 6 is ubiquitous (Fig. 2/24b). It is the first cement zone to occur both in the Blaen Onneu and Pwll-y-cwm Oolites of the Clydach area and elsewhere in the Oolite Group. A patchy zonation is usual but at the base of the Coral Beds well formed 'Fir-tree' zonation is found. This again is limited to the eastern half of the outcrop and corresponds to Area D of Zone 4 and the occurrence of second order zonation within Zone 5. Whether the coincidence of all these special features is by chance or not is unclear, but there seems to be 'something special' about the base of the Coral Bed in the eastern half of the outcrop.

The shaded area in Fig. 2/24b shows where the unusual, normally growth zoned Zone 6 cement occurs (Fig. 2/15a, b). The relative age of this cement with respect to other Zone 6 calcite is unclear. The reason for the limited distribution of this cement is unknown.

The limited occurrence of late Zone 6 cement and its frequent restriction to veins reflects the lack of pore space remaining at the time of its precipitation. The widespread, though limited, occurrence of late Zone 6 shows that its parent pore fluids were pervasive throughout the study area.

Zone 7

Like late Zone 6, the limited occurrence of Zone 7 (Fig. 2/25a) reflects lack of pore space available at the time of its precipitation. Again the widespread distribution shows that its parent pore fluids were pervasive throughout the study area. The change from calcite to dolomite precipitation must reflect a major change in pore water chemistry.

Discussion

From the above description of the distribution of the various cement zones a number of observations can be made.

1. there are two areas within the Oolite Group of the study area that are diagenetically distinct:-

   Area 1 - the Pwll-y-cwm Oolite to the top of the Blaen Onneu Oolite in the Clydach area, which contains the zonal sequence 1, 2b and 6;

   Area 2 - the rest of the Oolite Group, which contains the zonal sequence 2a, 3, 4, 5 and 6.

   The lateral transition between the two areas is achieved between Coed Pant-y-daren and Daren Odu, a distance of approx. 2 km. The vertical transition is more abrupt, occurring between the top of the Blaen Onneu Oolite and the top of the Clydach Beds. Some of the 'early' cements found within the Clydach Beds are similar to Zone 2b (Fig. 2/9b). The vertical transition is largely obscured by dolomitisation.

   The possibility exists that Zones 1 and 2a are laterally equivalent. At Coed Pant-y-daren Zone 2b is found between Zones 2a and 3. If this represents the entire precipitation

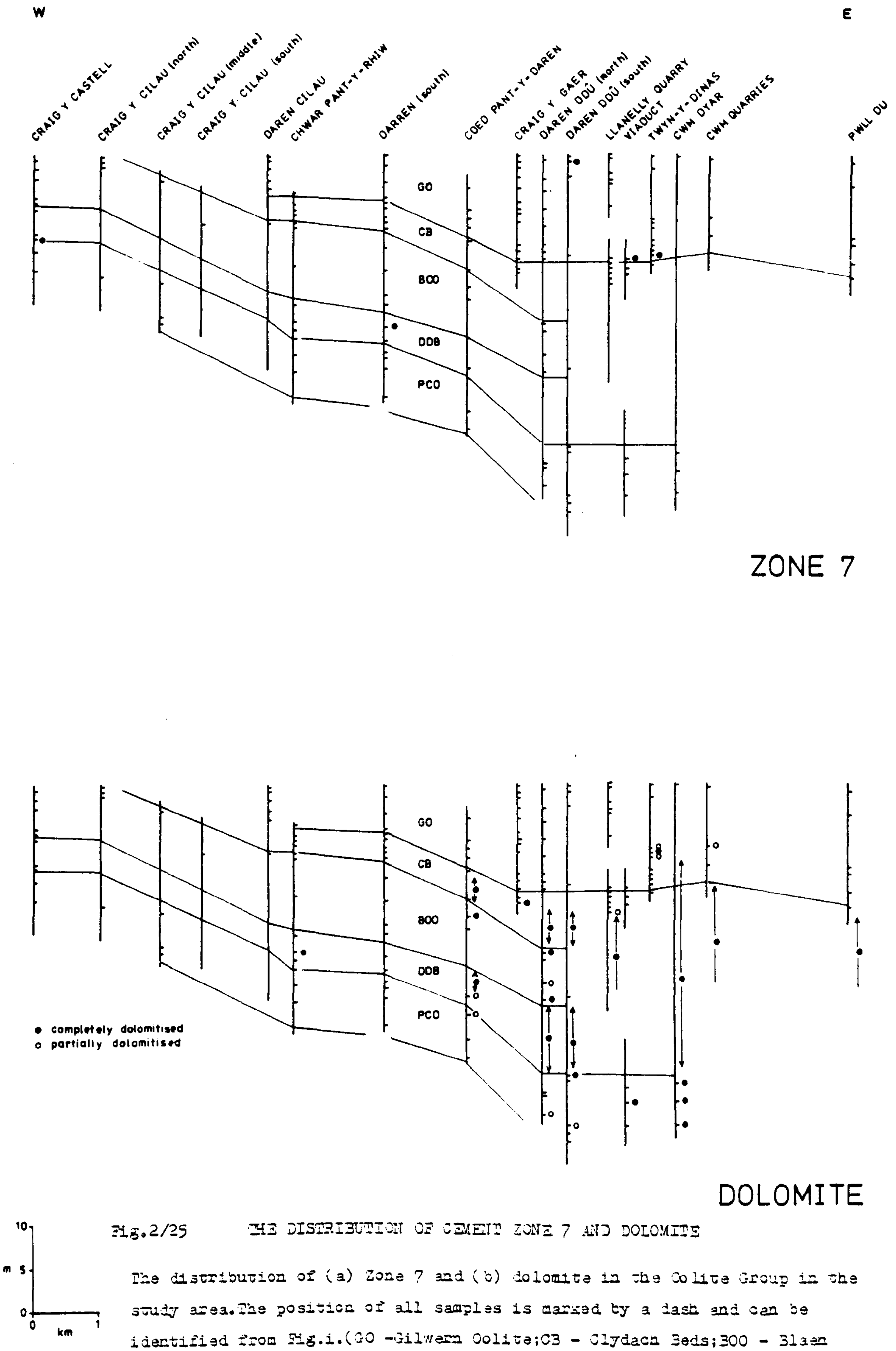


Fig.2/25 THE DISTRIBUTION OF CEMENT ZONE 7 AND DOLOMITE

The distribution of (a) Zone 7 and (b) dolomite in the Oolite Group in the study area. The position of all samples is marked by a dash and can be identified from Fig.i. (GO - Gilwern Oolite; CB - Clydach Beds; BOO - Blaen Onneu Oolite; DDB - Daren Ddu Beds; PCO - Pwll-y-cwm Oolite) event of Zone 2b, then there must have been a considerable period when cementation was occurring in Area 2 but not in Area 1; spanning the precipitation of Zones 3-5.

The first cement zone that the two areas have in common is Zone 6. Therefore the distinctive character of the two areas must have been lost prior to Zone 6 precipitation. It is known that a major phase of diagenetic sedimentation preceded Zone 6 precipitation. The fluids carrying this sediment may have flushed the entire Oolite Group in the study area, resulting in the replacement of the pore fluids in both areas.

The distribution of dolomitisation in the east of the study area is closely associated with Area 1 (Fig. 2/25b). Dolomitisation is thought to pre-date Zone 6 precipitation (see Chapter 4). The distribution of the dolomitisation may be controlled, or be controlling the unique chemical environment of Area 1;

2. the Coral Bed in the eastern half of the outcrop appears to be 'special'. The following factors set it apart from the rest of Area 2:
   a) Zone 2a contains abundant brightly luminescing calcite;
   b) Zone 4 occurs as well formed crystals showing characteristic changes in crystallographic form. The second order zonation pattern does not fit with that identified in the rest of the outcrop west of Coed Pant-y-daren;
   c) these are virtually the only rocks to contain Zone 5 consisting of alternating ferroan and non-ferroan second order zones. The number of second order ferroan zones increases eastwards;

d) this is the only place where 'Fir-tree' zonation is commonly found within Zone 6.

All these 'special' features disappear west of Coed Pant-y-daren, which is the western limit of features associated with Area 1. Prior to Zone 6 precipitation two diagenetic environments existed inthe Clydach area. Area 2 lay above Area 1, the transitional zone being only a few metres. The unusual features seen in the Coral Bed in the Clydach area may result from the mixing of the pore waters in these two areas. Unfortunately this explanation cannot be extended to explain the development of 'Fir-tree' zonation, since this formed after the distinction between the two diagenetic environments had been lost;

3. there appears to be a lateral change in Zone 4 cementation in the Pwll-y-cwm and Blaen Onneu Oolites between Craig y Castell and Daren Ddu. In the west of the study area, second order zones a, b and c are developed. As one moves eastwards the second order zones that are developed change to c and then c and d. East of Coed Pant-y-daren this is accompanied by a thinning of Zone 4. This shift in the position of the second order zones suggests that the focus of cementation moved progressively eastwards during the precipitation of Zone 4. It is not clear how the Zone 4 cements from the Gilwern Oolite fit into this picture. This may be partly explained by the factors considered in (2) above;

4. a problem exists with the identification of ferroan and non-ferroan calcite in Zones 3 and 5. Do these zones appear non-ferroan in some instances due to variations in iron content

of zones or is it a result of the limitations of the staining technique combined with small crystal size? The problem can only be resolved by detailed chemical analysis;

5. Zone 6 within the Gilwern Oolite between Pwll du and Daren Ddu is atypical, being well zoned. Similar Zone 6 is not found anywhere else in the Oolite Group. The origin of this unusual Zone 6 cannot be speculated on at this stage. However, it again highlights the unusual aspects of the cementation of this half of the outcrop;
6. the change from calcite to dolomite precipitation that occurs with the precipitation of Zone 7 must mark a major change in pore water chemistry;
7. substrate plays an important role in controlling the distribution of 'early' cements. Hence, Zone 2a is only found in rock with echinoderm fragments. Therefore it is absent from the Clydach Beds. Another factor that may play an important role in controlling the distribution of 'early' cements is the porosity and permeability of the sediment for the earlier cements are excluded from the finer grained sediments.

These ideas will be expanded and discussed further in Chapter 8.

2.4 Crystallography

The presence of abundant luminescing zones within the cement crystals of the Oolite Group has meant that it is possible to determine their crystallographic form. The following procedures were used to identify the crystallographic form of the cement crystals which changed at various stages of their growth:

1. measurement of the angle between terminal faces in sections

cut approx. parallel to the c-axis. This method is limited in its use since it gives no information regarding the rhombohedral or scalenohedral nature of the crystal. Rhombohedra and scalenohedra often have very similar terminal angles;

2. observation of the shape of sections cut approx. perpendicular to the c-axis. It is only possible to distinguish between scalenohedral and rhombohedral forms using this method. Scalenohedra have hexagonal cross-sections and rhombohedra have triangular cross sections. The hexagonal section through a scalenohedron is unique in possessing alternate large and small angles;

3. measurement of the angles between faces in sections cut approx. perpendicular to the c-axis, the calculation of the angle of the c-axis relative to the plane of the section using the universal stage and from this information the calculation of the crystallographic form using stereoscopic projection (Dickson, pers. comm.) This method gives the most specific information about the crystallographic form of a crystal. However, one major assumption is made; that the form under investigation is one of the 19 most common forms (Dana, 1932). Only if these cannot be matched with the data is one of the less common forms considered. Even this method may not give a unique answer. Some of the forms are so similar that with the errors inherent in this method (2-3^{o}) they cannot be resolved. It is important to know the angle of the section under investigation because different rhombohedra cut at different angles can give the same section. Also it makes the stereographic process less random.

In the hundreds of thin sections examined very few sections perpendicular to the c-axis, in the size range required, were found and these were predominantly through Zone 4 (this zone having the greatest thickness parallel to the c-axis). This is because the c-axes of the cement crystals predominantly lie perpendicular to the substrate and the largest crystals (from which it is possible to calculate the crystallographic form) occur within moulds and shelter cavities and so their c-axes are vertical. All sections were cut in the vertical plane, hence the overwhelming majority of crystals are sectioned parallel to their c-axis. Also, difficulty has been encountered using some of the suitable sections because the crystals have developed abundant deformation twin lamellae making them unsuitable for orientation on the universal stage.

The crystallography of the cements found in the Oolite Group is outlined below:

Zone 1

This is best seen as spires in syntaxial overgrowths on echinoderm fragments. The spires have acute terminations (approx. 40^0 (Fig. 2/13a-c). Only tiny sections through Zone 1 perpendicular to the c-axis have been found. This indicates a rhombohedral form. This, together with the angle between the faces in the sections cut parallel to the c-axis, means that it possibly has a $\{40\bar{4}1\}$ form.

Zone 2

Zone 2a has triangular cross-sections when cut perpendicular to the c-axis (Fig. 2/26a), hence it is rhombohedral. The small number of such sections and the diffuse, irregular nature of their outer margin makes it impossible to work out the exact form present.

Fig.2/26 THE CRYSTALLOGRAPHY OF ZONES 2a,3 AND 4

a)Sections through Zones 2a - 4 cut perpendicular to the c-axis.Triangular cross-sections indicate rhombohedral form.Sample 21664.

b)Sections through Zones 3 - 5 cut perpendicular to the c-axis.Triangular cross-sections indicate rhombohedral form.Sample 22358.

c)Sections through Zones 3 and 4 in a variety of directions.In sections cut approx. parallel to the c-axis the direction of the c-axis is indicated. Sample 18337.

d)Section through Zone 3 approx. perpendicular to the c-axis.There is no evidence of changing form during growth.Sample 17854.

e)Zone 4 cements showing scalenohedral cross-sections (S) in sections cut perpendicular to the c-axis.Sample 18346.

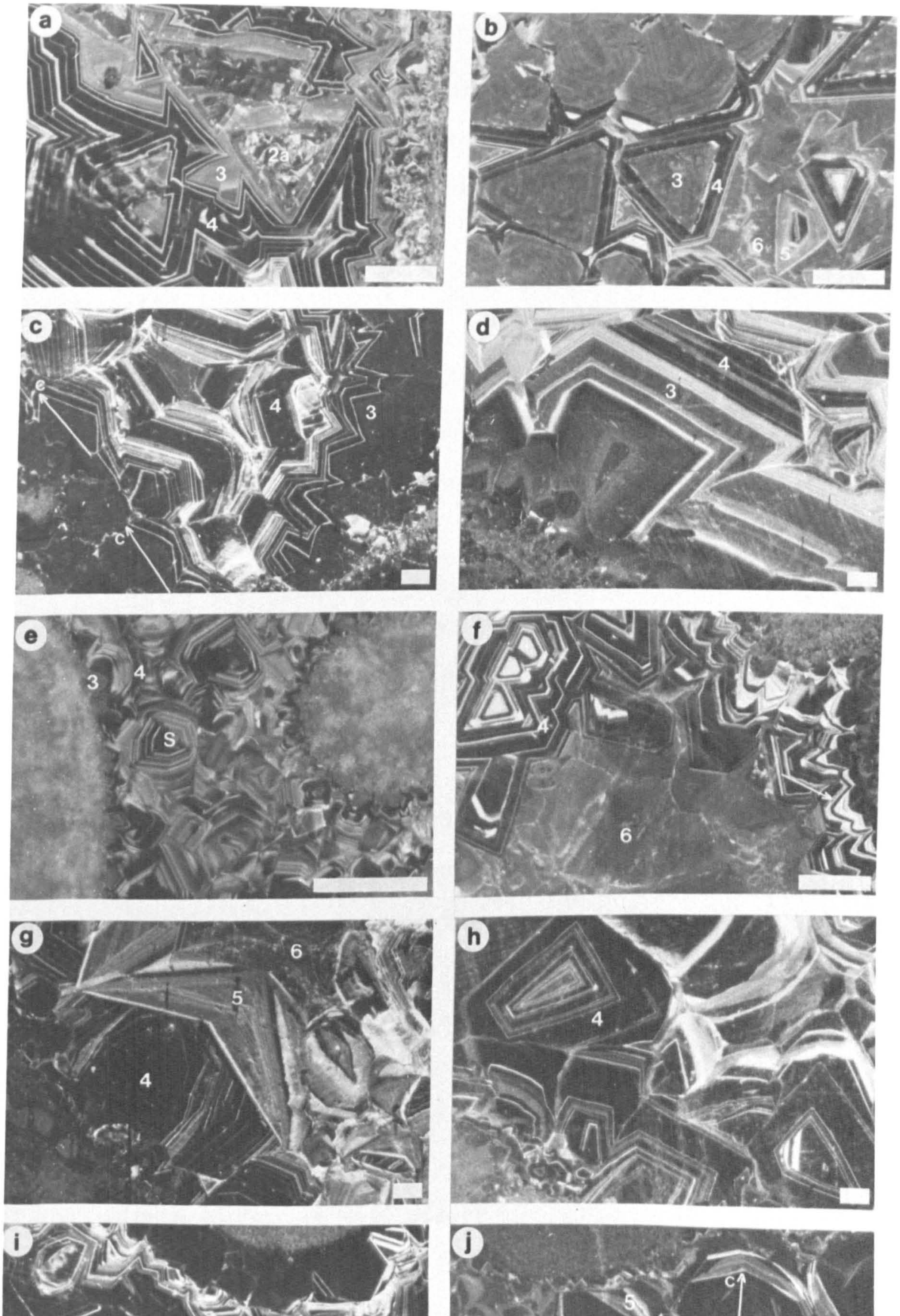
f)Sections through Zone 4 cut approx. perpendicular and parallel to the c-axis. Triangular cross-sections indicate rhombohedral form.In sections cut parallel to the c-axis changing form is apparent (arrow).Sample 17872.

g)Section cut parallel to the c-axis showing Zones 4 - 6.During its growth Zone 4 has changed in form.Sample 18304.

h)Section through Zone 4 cut perpendicular to the c-axis.The triangular cross-section indicates rhombohedral form.Sample 18304.

i)Changing crystal form in Zone 4b.This involves the alternation between obtuse and acute terminations.Sample 20550.

j)'Lozenge-shaped' Zone 4 crystals.The c-axis lies perpendicular to the substrate as indicated.The elongation of the Zone 4 crystal was at a high angle to the c-axis.Sample 18306.


a
2a
3
4
b
3
4
6
5
c
e
4
3
c
d
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3
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f
4
6
g
6
5
4
h
4
i
4
j
5
4
c

The faces are more or less parallel to those of Zone 3 forms, suggesting that the forms of Zones 2a and 3 are similar. This would mean that the form of Zone 2a was probably the $\{02\bar{2}1\}$ rhomb.

Zone 3

The triangular cross-sections of Zone 3 (Fig. 2/26a-d) indicate that it has a rhombohedral form. $\{02\bar{2}1\}$ is the most usual form, although $\{10\bar{1}1\}$ may also occur. The form of Zone 3 has not been found to change during its growth (Fig. 2/26d).

Zone 4

The cements of Zone 4 are very variable both in their secondary zonation pattern and in the crystallographic forms developed. Zone 4 cements will be considered in the areas outlined in Fig. 2/23b.

Area A - Cements in Area A consist of a combination of rhombohedra and scalenohedra (Fig. 2/26e). The specific forms have not been identified. There appears to be no change in the form during growth. Scalenohedra decrease in importance eastwards.

Area B - There is little evidence of changing form within this area. This may partly be due to the lack of brightly luminescing third order zones. The main form present is the $\{02\bar{2}1\}$ rhombohedron. In some crystals an obtuse terminal form is also present ($\{01\bar{1}2\}$?).

Area C - Zone 4 cements are again rhombohedral. Changing crystal form may be evident in Zone 4d (Fig. 2/26f). It is not possible to work out the forms involved, but they all appear to be rhombohedral. The changes in form involve the alternation between acute and obtuse forms.

Area D - The well formed crystals of the Coral Bed show characteristic changes in crystal form (Fig. 2/26g). The forms present are illustrated in Fig. 2/28c. The forms consist of the $\{02\bar{2}1\}$ and $\{01\bar{1}2\}$ rhombohedra (Fig. 2/26h) and prisms. The prism faces increase in importance during the growth of Zone 4. The outer margin of Zone 4 outlines a prism with a $\{01\bar{1}2\}$ termination. West of Craig y Gaer these variations are lost. Changes in form still occur but are restricted to the outer portion of Zone 4 (Fig. 2/26i). These changes still involve the alternation between obtuse and acute forms however.

Area E - In this area $\{01\bar{1}2\}$ rhombohedra are again well developed. However, in this area they occur as a closed form, not in association with prisms as in Area D. The maximum growth direction in $\{01\bar{1}2\}$ rhombs is at a high angle to the c-axis; this results in their 'lozenge-like' shape mentioned in 2.3 (Fig. 2/26j). The lack of second and third order zonation within Zone 4 makes it impossible to establish any earlier crystallographic forms that might have been present, but Zone 4 cements appear to have undergone similar changes to those seen in Area D.

Area F - Both scalenohedra and rhombohedra are present in this area (Fig. 2/27a). None have been positively identified. The alternation between acute and obtuse forms again occurs (Fig. 2/27b).

Zone 5

Where Zone 5 consists of a single, dull luminescing zone it forms an acute termination over the final obtuse termination of

Fig.2/27 THE CRYSTALLOGRAPHY OF ZONES 4,5 AND 6

a)Sections through Zones 3,4 and 6.The brightly luminescing line within Zone 4 has a scalenohedral outline (S).Sample 17857.

b)Zones 3 and 4.The arrow shows where changes in crystal form are occurring. Sample 17844.

c)Sections through Zone 5 cut perpendicular to the c-axis.Triangular cross-sections indicate rhombohedral form.Sample 22358.

d)Zone 5 consists of alternating second order zones consisting of dull luminescing ferroan calcite and dominantly non-luminescing non-ferroan calcite.The former produces acute terminations,the latter obtuse terminations Sample 17862.

e)Zone 6 showing 'normal'growth zonation.The growth zones have scalenohedral cross-sections (S).Sample 17352.

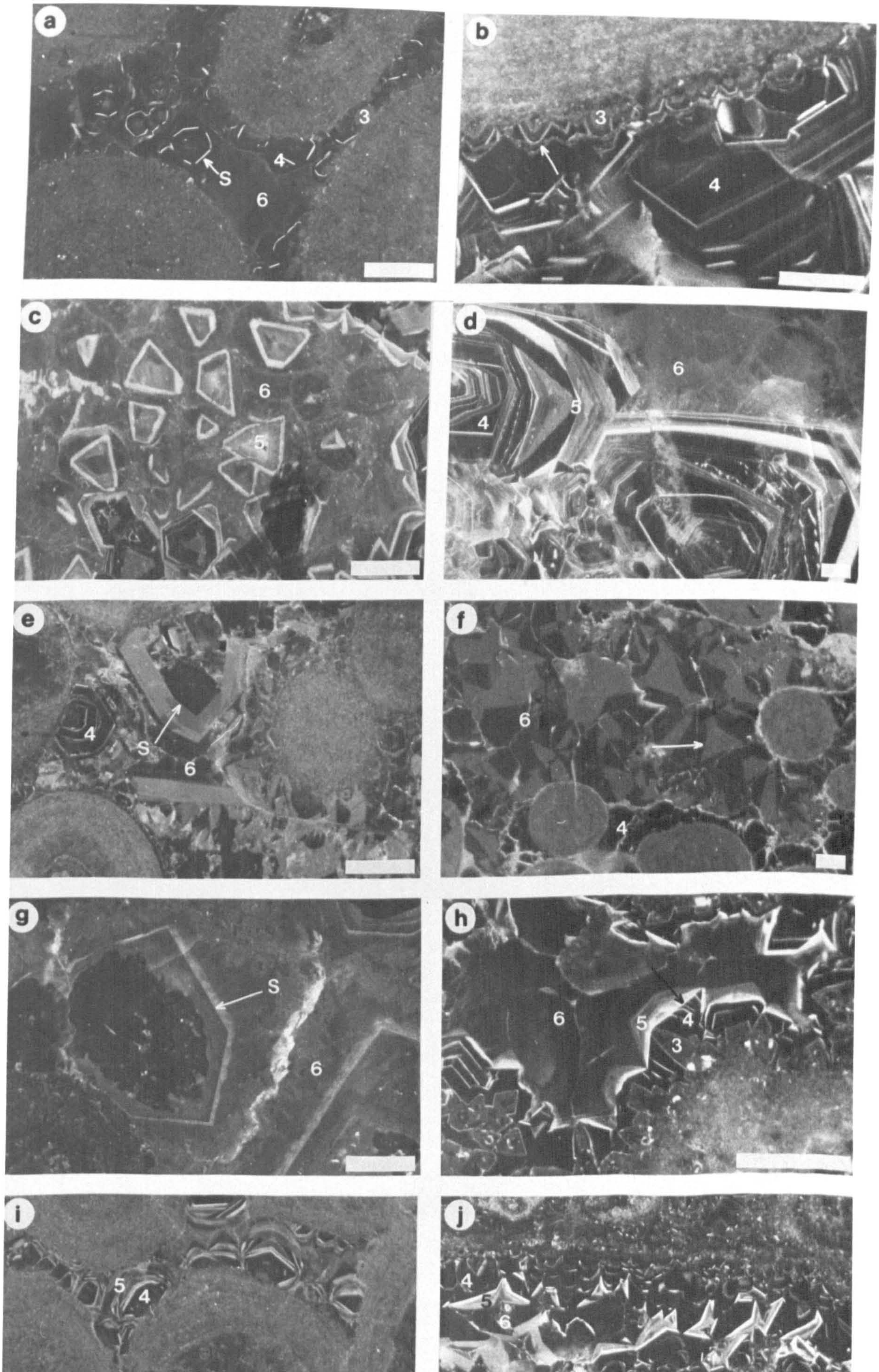
f)Zone 6 showing a patchy distribution of zones.Occassionally areas reminiscent of 'Fir-tree' zonation are found (arrow).Sample 17865.

g)Late Zone 6 often displays scalenohedral form.The scalenohedron(S)has the $\{21\bar{3}1\}$ form.Sample 20592.

h)Changing crystal form can result in the truncation of growth zones (arrow). Sample 17868.

i)'Lozenge-shaped' Zone 4 crystals are oriented with their c-axes perpendicular to the substrate and their maximum growth direction approx. parallel to the substrate.Sample 18036.

j)Zone 4 crystals at the top of the filled cavity are oriented with their c-axes approx. parallel to the substrate and their maximun growth direction approx. perpendicular to the substrate.Sample 17852.



a
3
4
S
6
b
3
4
c
6
5
d
6
4
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e
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S
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4
g
S
6
h
6
5
4
3
i
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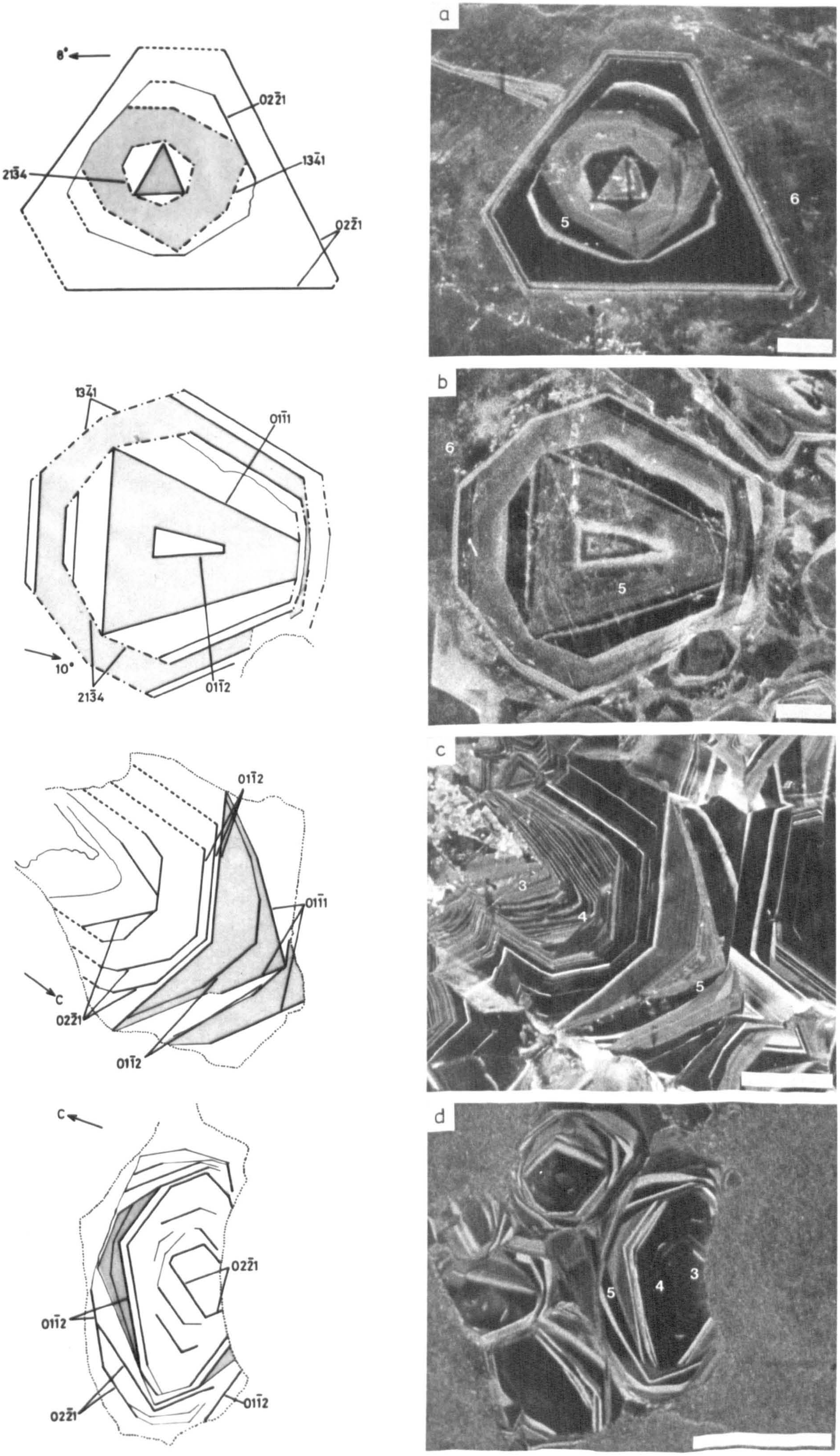
4
j
4
5
6

Fig.2/28 CHANGING CRYSTALLOGRAPHIC FORM IN CEMENT CRYSTALS FROM THE CORAL BED

Four cement crystals from the Coral Bed are illustrated on the right.(a) and (b) are sections approx. perpendicular to the c-axis.(c) and (d) are sections approx. parallel to the c-axis.During their growth the cement crystals illustrated have changed their crystallographic forms.Some of the forms developed are identified on the sketches on the left.The direction of the c-axes and their inclination from the vertical,if known,are shown.(------- - prism faces;·-·-·-·- - scalenohedral faces; ——— - rhombohedral faces; ——— - unidentified).Samples 18303,17862,18325,18306.



8°
$02\bar{2}1$
$21\bar{3}4$
$13\bar{4}1$
$02\bar{2}1$
a
5
6
$13\bar{4}1$
$01\bar{1}1$
10°
$21\bar{3}4$
$01\bar{1}2$
b
6
5
$01\bar{1}2$
$01\bar{1}1$
c
$02\bar{2}1$
$01\bar{1}2$
c
3
4
5
c
$02\bar{2}1$
$01\bar{1}2$
$02\bar{2}1$
$01\bar{1}2$
d
5
4
3

Zone 4. Sections perpendicular to the c-axis are rare, probably because Zone 5 forms a low percentage of the total cement. Those found indicate that it is rhombohedral (Fig. 2/27c). The one determination of the crystal form possible showed the $\{10\bar{1}1\}$ rhomb to be present. This cannot be the predominant form as it would produce an obtuse termination to the crystals. It may be a subsidiary form occurring at the tip of the crystal.

Where Zone 5 consists of a number of alternating ferroan and non-ferroan second order zones the situation is more complicated. The ferroan second order zones form acute terminations and the non-ferroan second order zones form obtuse terminations, similar to those occurring at the outer edge of Zone 4 (Fig. 2/27d). Scalenohedra as well as rhombohedra can be identified (Fig. 2/28).

Zone 6

Staining and CL show that it is unusual for this zone to show 'normal' growth zonation. Normal growth zoning is restricted to the area shaded in Fig. 2/24b and to late Zone 6 calcite. The cements that occur in the shaded area show a number of forms, including scalenohedra (Fig. 2/27e). Late Zone 6 cements are also mainly scalenohedra, the $\{21\bar{3}1\}$ form has been identified (Fig. 2/27g).

Three unusual types of Zone 6 have been found:

1. 'Fir-tree' zoned;
2. 'patchily' zoned;
3. 'sutured' spar.

These are described in turn below.

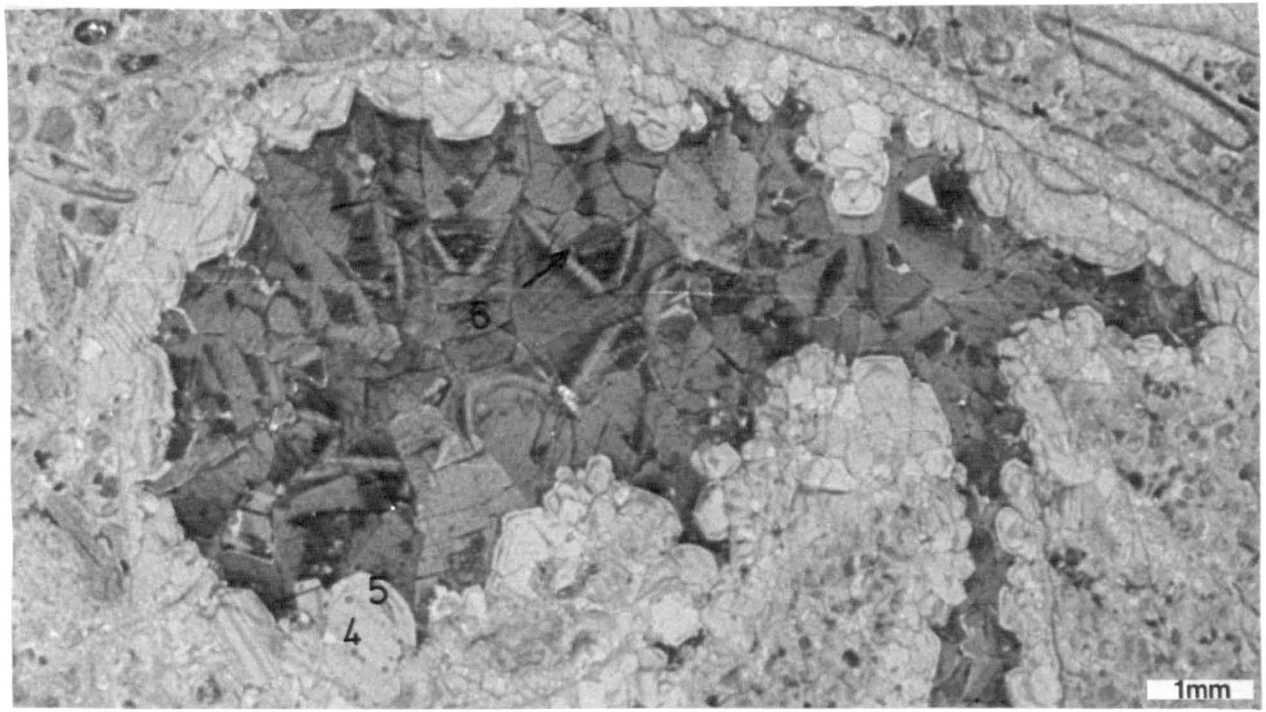
'Fir-tree' zonation

This is best seen in samples from the Coral Bed in the eastern portion of the outcrop (Fig. 2/24b). To the best knowledge of the author this is the first reported occurrence of such a zonation pattern in calcite. It involves the intergrowth of two different ferroan calcites with distinct CL and staining properties. In sections cut parallel to the c-axis a series of stacked triangular areas, apex pointing in the direction of growth, extend from the outer limit of Zone 5 and lie parallel to the c-axis (Fig. 2/29). The triangular areas, not always perfectly formed, tend to increase in size in the direction of growth. The rest of the crystal is made up of the less ferroan of the two calcites. The variation in the Fe^{2+} content of the calcite is, on occasions, accompanied by variations in the density of solid inclusions. Thin bands of the more ferroan calcite may extend back from the triangular areas, inclined at the same angle as the triangle's apical faces (Fig. 2/29a). Where these are common it suggests a more 'normal' zonation pattern. In sections cut at low angles to the c-axis a more complicated pattern is seen (Fig. 2/30). The zonation pattern reflects the trigonal symmetry of calcite. Three 'arms' extend from the middle of the crystal, 120^{o} apart. Each consists of stacked triangular areas increasing in size in the direction of growth. The number of triangular areas in the 'arms' is variable. This is thought to be related to varying periods of growth.

A possible growth scheme is suggested in Fig. 2/31 to explain the development of this zonation pattern. This is not meant to be a definitive statement as to how this type of zonation pattern developed, only a suggestion as to how the patterns seen can be simulated. The following assumptions were made in the construction of Fig. 2/31:

Fig.2/29 'FIR-TREE' ZONATION IN CRYSTALS CUT APPROXIMATELY PARALLEL TO THEIR C-AXES

(a) and (b) Transmitted light photomicrographs of stained thin sections showing Zone 4 to 6 cement crystals, cut approx. parallel to their c-axes, filling a gastropod mould and a bivalve mould respectively. Early Zone 6 cement consists of two ferroan calcites, one appearing darker than the other. The darker of the two occurs in a series of stacked triangular areas which increase in size in the direction of growth. Occasionally lines of the darker ferroan calcite extend back from the triangular areas (arrow) suggesting a more 'normal' growth zonation. Sample 17862.


6
5
4
1mm


2
4
6
5
1mm

Fig.2/30 'FIR-TREE' ZONATION IN CRYSTALS CUT APPROXIMATELY PERPENDICULAR TO THEIR C-AXES

Transmitted light photomicrograph of a stained thin section showing Zone 4 to 6 cement crystals filling a gastropod mould.The bulk of the mould is filled with Zone 6 cement crystals that are cut approx. perpendicular to their c-axes.Zone 6 ferroan calcite cement consists of two ferroan calcites, one appearing darker than the other.The darker of the two extends from the middle of the crystal outwards in three arms approx. 120° apart (arrows). These arms have a serrated outline.At the base of the mould there is a layer of geopetal diagenetic sediment (S) overlying Zone 5 calcite.Within this the cement crystals have sutured contacts.

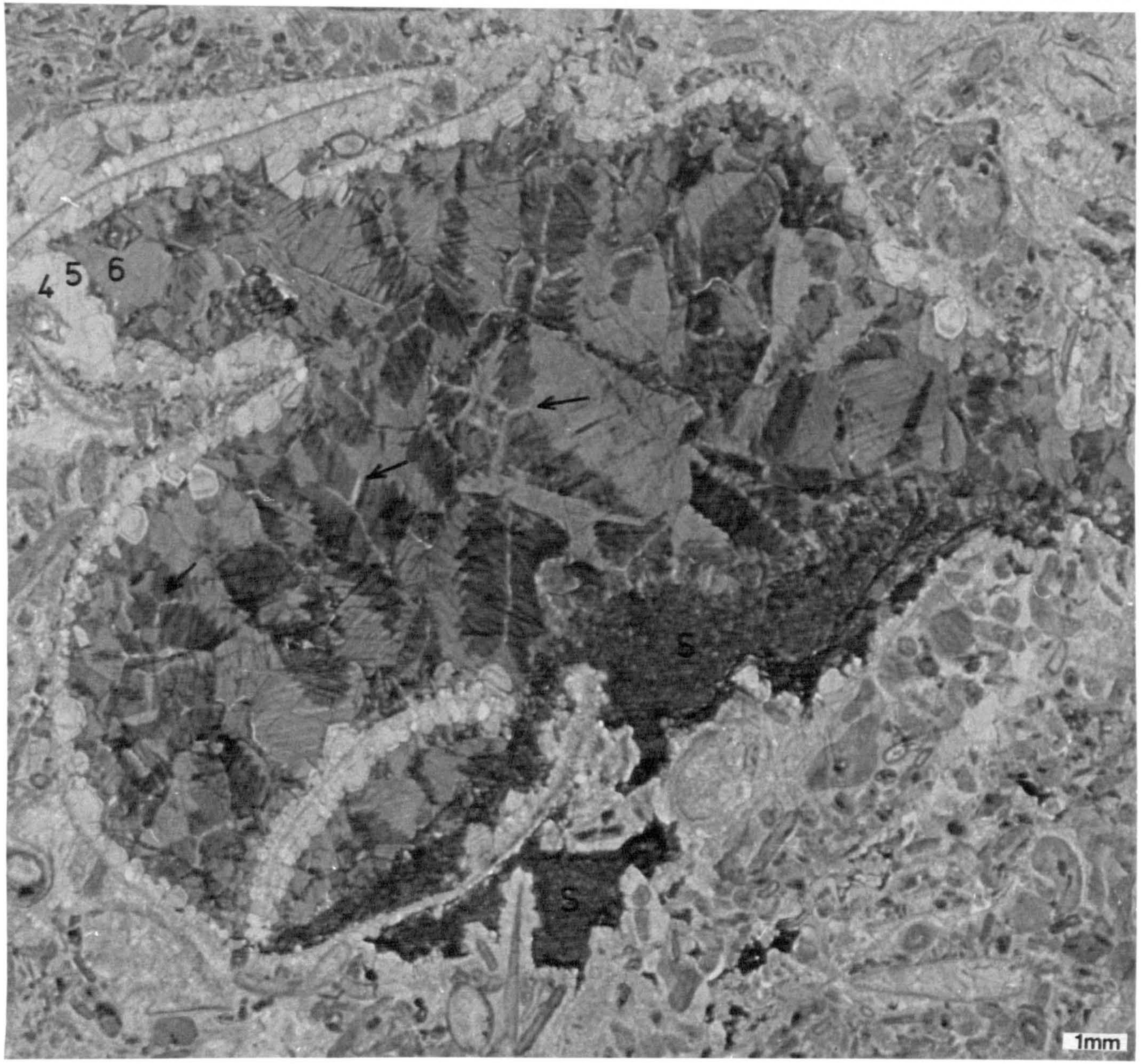
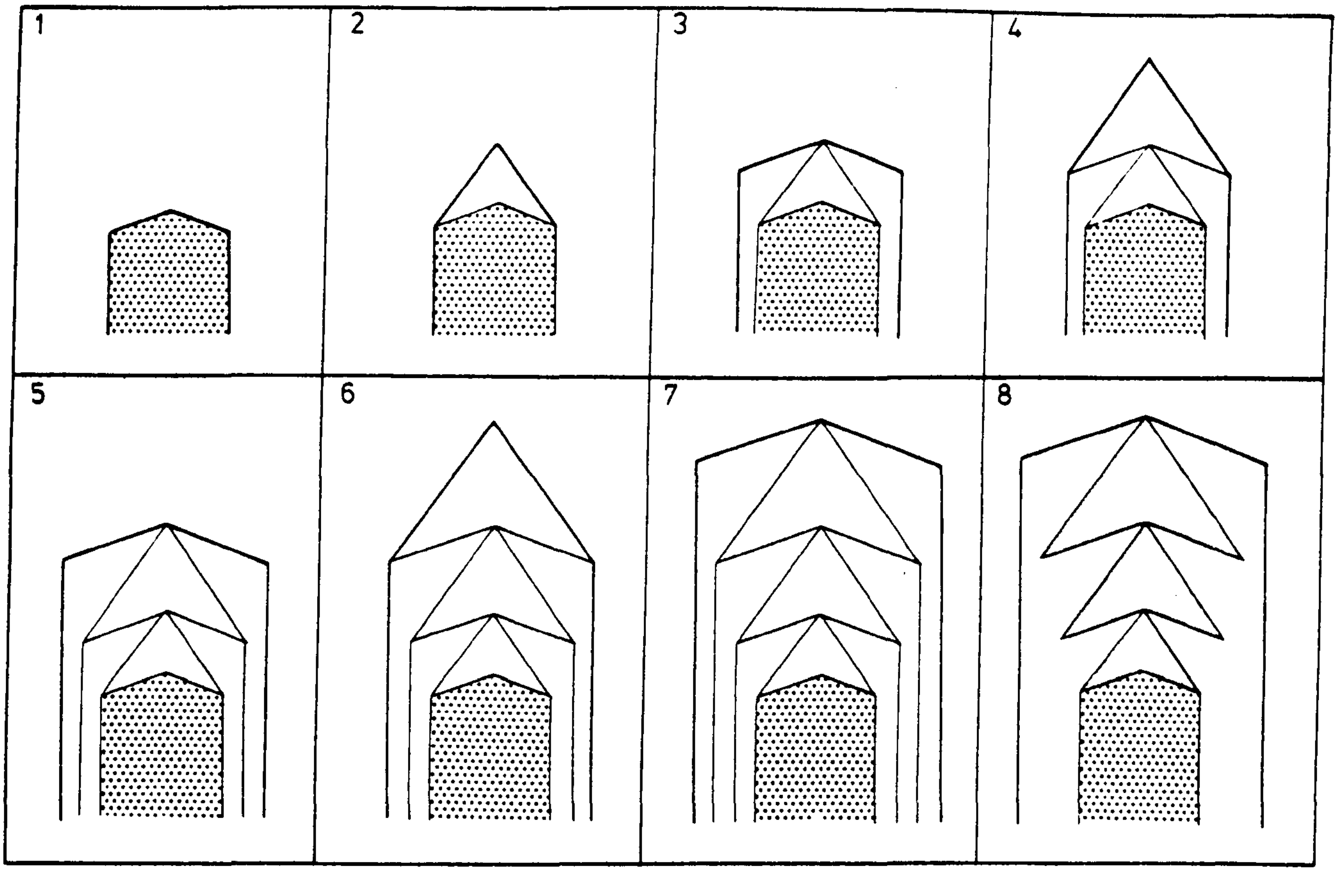

4 5 6
S
S
1mm

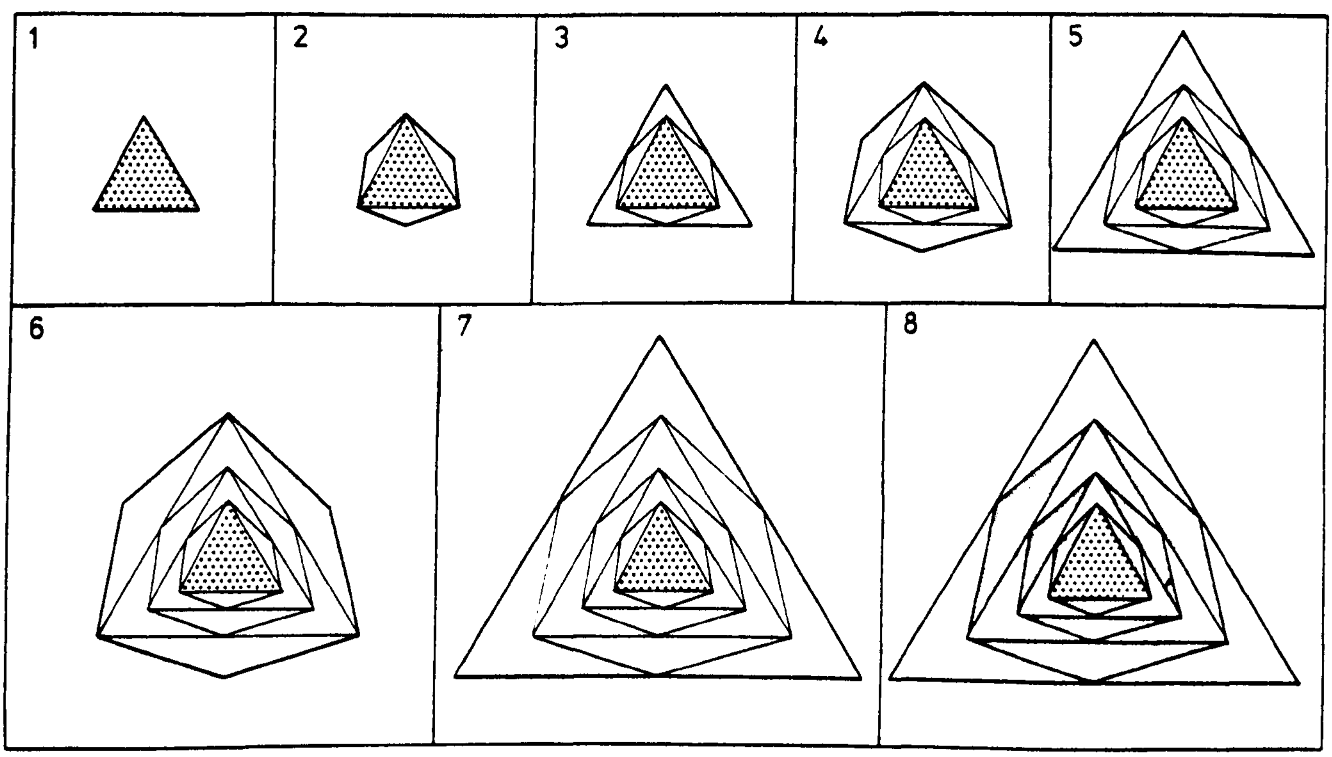
Fig.2/31 THE DEVELOPMENT OF 'FIR-TREE' ZONATION

Diagram showing the development of patterns similar to those seen in 'Fir-tree' zonation in sections cut parallel and perpendicular to the c-axis. The pattern is produced by the alternate development of obtuse rhombohedra and acute scalenohedra. The resulting pattern is illustrated in 8.

SECTION PARALLEL TO C-AXIS



SECTION PERPENDICULAR TO C-AXIS



1. sections were cut either parallel to the c-axis through the apex of the crystal, or perpendicular to the c-axis passing through the termination of Zone 5 calcite;
2. there is no competition for space during the growth of the crystal;
3. growth continues until and does not exceed that required to develop a new termination;
4. there is no precipitation on prism faces during the development of acute terminations.

The system suggested in Fig. 2/31 requires the alternate development of scalenohedra and rhombohedra which have acute and obtuse terminations respectively. This system is based on the changes in crystal form that are seen to occur within Zone 5 where it consists of alternate ferroan and non-ferroan second order zones (Fig. 2/28). A similar zonation pattern has been described in brookite (Grigor'ev, 1965). Here it is due to the variation in the degree of development of the 001 pyramid.

Staining and CL suggest that at least the Fe^{2+} (and perhaps the Mn^{2+}) content of each of the two ferroan calcites is constant. This is surprising since each ferroan calcite does not result from a single precipitation event. If the variation in Fe^{2+} between the two ferroan calcites were due to oscillating Fe^{2+} content in the pore water from which they were precipitated some variation would be expected in each of the two ferroan calcites. Perhaps the Fe^{2+} content of the calcite is controlled by the crystallographic form being precipitated, i.e. the distribution co-efficient controlling the incorporation of Fe^{2+} into calcite is a function of crystallographic form. The uptake of trace elements is known to be controlled by crystallographic form in certain minerals, e.g. topaz, pyroxene, tourmaline, giving rise to sector zoning (Grigor'ev, 1965).

'Patchy' zonation

As with 'Fir-tree' zonation two distinct ferroan calcites are again involved, but in this case they have a patchy distribution (Fig. 2/27f). Occasionally there are small areas that are reminiscent of 'Fir-tree' zonation. A recrystallisation origin is improbable as none of the other cement zones, occurring in the same crystal, show any signs of recrystallisation and retain their original zonation patterns. It is thought that 'patchy' zonation results from the imperfect development of 'Fir-tree' zonation.

'Suture' spar

Some of the ferroan calcite crystals of Zone 6 have sutured contacts. Such a fabric only occurs at the base of large, former cavities and has an abrupt, horizontal upper surface above which Zone 6 crystals have non-sutured contacts (Fig. 2/30). Crystals are continuous across the boundary between the two types of fabric. The ferroan calcite with sutured contacts contains abundant inclusions of fine grained, terrigenous material. Despite its sutured contacts it is thought that this calcite is a primary precipitate, not the result of recrystallisation. Its fabric is the result of the poikilotopic growth of calcite crystals within terrigenous, diagenetic sediment. The series of events leading up to the formation of the sutured contacts is listed below.

1. calcite crystals nucleate within terrigenous material and grow outwards;
2. the calcite crystals encounter terrigenous grains and split to pass around them;
3. the various branches of the crystals grow at slightly different rates so that the crystals have irregular margins;
4. this process continues until adjacent crystals meet. Since the growth rate is not constant around each crystal the boundaries between crystals will be irregular.

Zone 7

The crystallography of saddle dolomite, similar to that found in Zone 7, has been described by Radke & Mathis (1980).

How are changes in crystallographic form achieved ?

Cement crystals from the Oolite Group commonly change their crystallographic form during growth. This often takes the form of alternating development of acute and obtuse terminations. The numerous second and third order zones, visible with CL, makes it possible to trace not only the crystallographic forms developed but also how the changes in form were achieved.

Fig. 2/32 shows the progressive development of two cement crystals from the base of the Gilwern Oolite. New forms develop at the expense of older forms. This is achieved by the crystal faces of the older forms becoming progressively shorter with each layer of calcite precipitated. The rate at which the length of a face is reduced will control the angle and hence the form of the face that is developed. A natural result of this process is the truncation of CL zones along crystal faces (Fig. 2/27h). It could be construed that this truncation is the result of etching

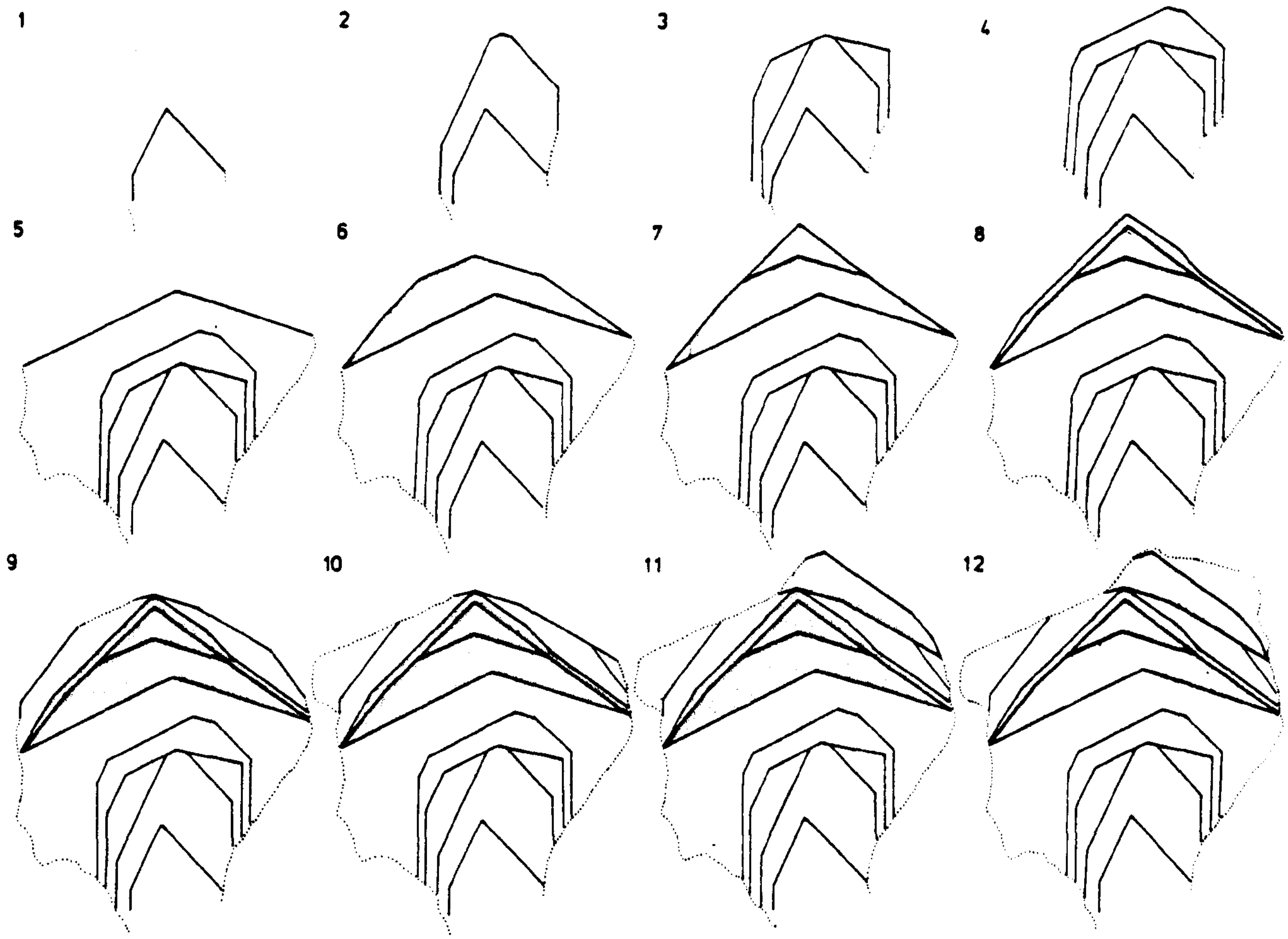
Fig.2/32 THE GROWTH HISTORY OF TWO CALCITE CRYSTALS

The crystals considered below are illustrated in Fig.2/23c and d.The stages in the growth of these two calcite crystals are as follows:

a)1. in the initial stages of growth the crystal has an acute,rhombohedral termination.(Zone 3)

2. two new forms begin to develop by the shortening of the terminal faces at both ends.The rate of shortening controls the new forms developed.(Zone 4)
3. this process continues and the new faces become dominant.They are a prism and an obtuse rhombohedral termination.During this stage growth only occurs perpendicular to the c-axis.One of the results of the changing form is that growth zones truncate at the new terminal faces.(Zone 4)
4. once the new terminal face is well developed growth resumes parallel to the c-axis,but the maximum growth direction is still perpendicular to the c-axis.(Zone 4)
5. the onset of competative growth (dotted lines mark compromise boundaries between crystals) means that good prism faces are lost and the terminal face is the only form left,this is an obtuse rhombohedron.(Zone 4)
6. the chemistry of the calcite changes (shading indicates ferroan as opposed to non-ferroan calcite) and so does the form of the termination.This is achieved by the continued precipitation of the same form of termination as seen in 5,but the faces become progressively shorter,retracting at both ends.The rate and position at which shortening occurs controls which new forms develop.Growth only occurs parallel to the c-axis.(Zone 5)
7. this process continues and an acute termination is developed,this consists of several forms.(Zone 5)
8. once the termination is complete calcite is precipitated on it parallel to the terminal faces.(Zone 5)
9. the chemistry of the calcite reverts back to being iron-free.This is accompanied by a change in the form of the termination.This is achieved by the continued precipitation of the acute terminal faces,but these are progressively shortened at both ends so that a prism and an obtuse termination begin to develop.(Zone 5)
10. this process continues.Growth zonation can be seen to be truncated at the obtuse termination as in 3.There is now little space in which the crystal can grow,so only one half of the new obtuse termination is properly developed.It is made up of two forms.
11. the chemistry of the calcite changes again (a change similar to that which occurred in 6).The termination becomes more acute.
12. the chemistry of the calcite changes again and the final pore space is filled.

b)Similar changes to those described for (a) can be seen in (b),with one major exception - prism faces do not develop.This leads to the 'lozenge-shaped' nature of the crystal .As a result of the changing crystallographic forms developed the crystal changes from length-fast to length-slow during its growth.It starts as length-fast(1),then becomes length-slow(2).With the development of an acute termination(4 and 5) it may again become length-fast. An obtuse termination again is developed(6 to 8) and the crystal is again length-slow.In some cases competative growth results in a length-fast crystal irrespective of the forms developed.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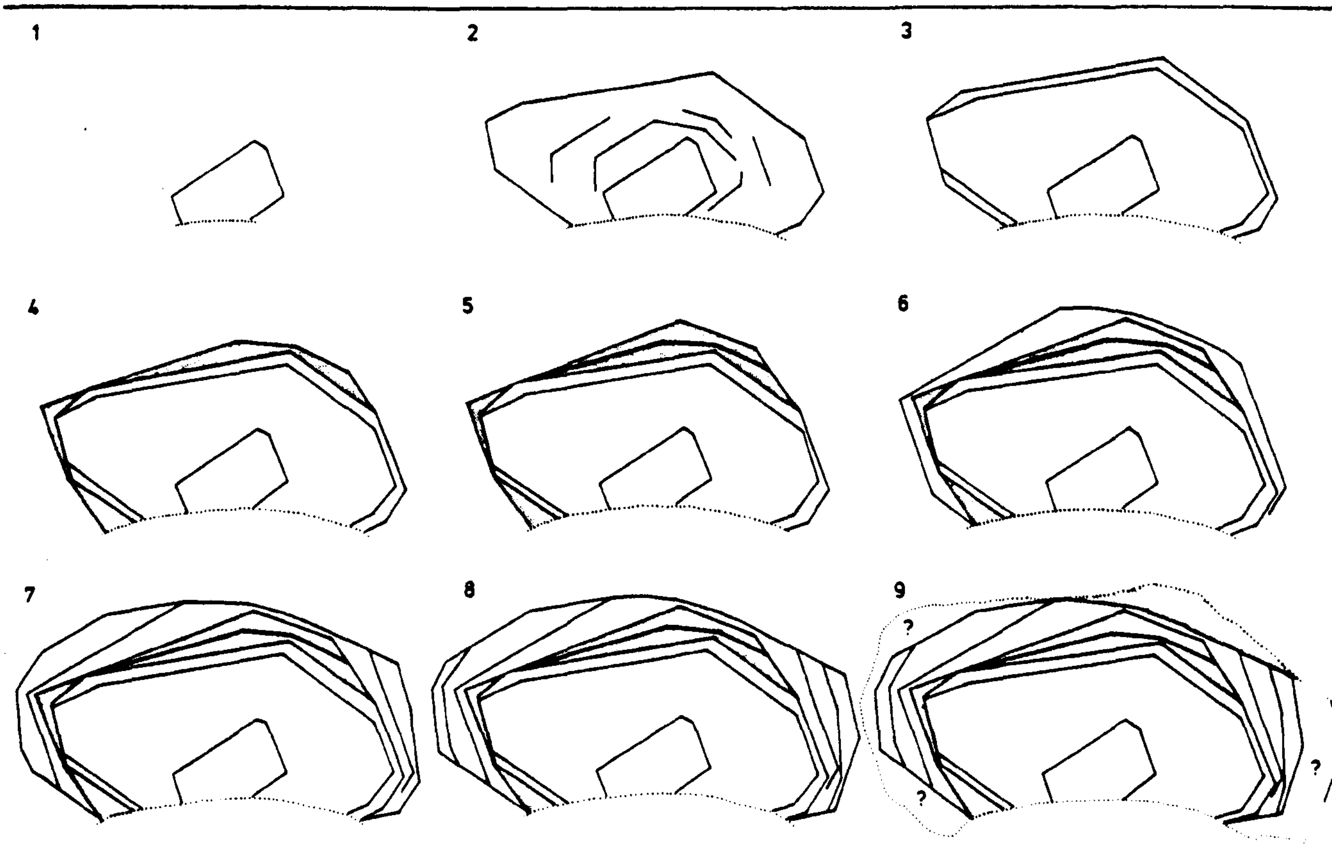
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rather than changing form. This is not thought to be the case since solution features are extensively developed in the Oolite Group and are manifested as fretted surfaces and holes in crystals (see Chapter 3).

<u>What causes changes in crystallographic form?</u>

There are numerous factors that can affect the crystallographic forms that develop in calcite crystals (Buckley, 1951; Kostov, 1968 p. 534). Some are listed below.

1. chemical impurities;
2. trace elements;
3. degree of saturation;
4. rate of growth;
5. temperature;
6. pressure.

It is difficult to ascribe a precise cause to the changes seen. Folk (1974) pointed out the importance of Mg^{2+} and to a lesser extent Na^{2+} in controlling the forms of calcite.

In Zone 5 the complex acute forms which include scalenohedra, are associated with the presence of Fe^{2+} in the calcite lattice. This does not mean that Fe^{2+} is responsible for the development of this particular form. Indeed, Zone 3 cements are also ferroan but they form simple rhombohedra. It may be that some other factor also altered when the change from non-ferroan to ferroan calcite occurred in Zone 5 and this was responsible for the change in form. Further speculation is pointless without information about the trace element variations occurring during the growth of the crystals. Even this may not be enough to resolve the problem, especially if the cause is physical rather than chemical.

Length-fast versus length-slow calcite

Length-slow calcite has been considered to be the result of in situ replacement (Lindholm, 1972, 1974; Folk & Asseretto, 1976; Kendal & Broughton, 1977; Kennedy et al., 1978). Dickson (1978) pointed out that the criteria that are commonly used to recognise cements, which require that cements are length-fast are not necessarily correct. Notably, the c-axis does not have to lie perpendicular to the ~~c-axis~~ substrate.

In the Oolite Group length-slow crystals have developed with their c-axes perpendicular to the substrate at certain times during diagenesis. The low nucleation density of cement crystals on allochems, especially within the Gilwern Oolite, has meant that during much of the growth history of the crystals (as far as Zone 6) there has been no competition for growing space and the crystals have extended, unhindered, parallel to the substrate. The 'lozenge-shaped' crystals of Zone 4 are often like this (Fig. 2/27i). Where the nucleation density was higher competitive growth occurred at a much earlier stage and crystals whose maximum growth direction lay perpendicular to the substrate thrived at the expense of those in which it did not. This is the situation described by Dickson (1978), (Fig. 2/27j).

Some cement crystals have alternated through their development, between length-fast and length-slow. In the first stages of growth this is a reflection of changing crystallographic form. However, with the onset of competitive growth, the length-fast habit prevails since the c-axes predominantly lie perpendicular to the substrate and further growth can only occur in this direction.

2.5 Crystal deformation

Many of the larger cement crystals of the Oolite Group show undulose extinction and contain abundant, closely spaced twin lamellae. Both of these features suggest that the crystals have been strained. The lack of twin lamellae and undulose extinction in the smaller crystals may be due to the accommodation of strain by movement along their crystal boundaries. This process appears to have been insufficient to relieve the strain in the larger crystals due to their smaller surface area/volume ratio, with the resulting internal deformation of the crystals. This is accomplished by the development of deformation twin lamellae (Turner, 1954). Twinning can result from the application of either tectonic or overburden pressure. The number of twin lamellae developed increases with increasing depth of burial (Friedman & Heard, 1974), the inverse relationship being true for the spacing of the twin lamellae developed. Friedman (1975) describes widely spaced twin lamellae developed in Pleistocene limestones, whereas the twin lamellae described by Borak & Friedman (1981) from approx. 9 km depth are very closely spaced.

Borak & Friedman (1981) describe twin lamellae that are often offset by the development of a younger cross cutting set of twin planes and also curved twin planes. The latter is commonly observed in the Oolite Group (Fig. 2/33c,d) cements, but the former is virtually absent (Fig. 2/33b). Displacement has occurred along twin planes and is revealed by CL (Fig. 2/33a,c,e,g). The chemical zonation shown by the CL is displaced stepwise by the twin lamellae. There is no degrading recrystallisation along twin planes as described by Voll (1960), Wardlaw (1962) and Borak & Friedman (1981).

Fig.2/33 CRYSTAL DEFORMATION

a)Growth zonation offset by two sets of twin lamellae,A and B.Sample 17869.

b)Transmitted light photomicrograph of the area shown in (a).The two sets of twin lamellae are identified.Sample 17869.

c)Growth zonation 'smeared out' as a result of deformation.Within Zone 6 there are areas of brightly luminescing calcite oriented parallel to the two sets of twin lamellae present.Sample 17880.

d)Transmitted light photomicrograph of the area shown in (c).Sample 17880.

e)Growth zonation 'smeared out' as a result of deformation.Sample 18335.

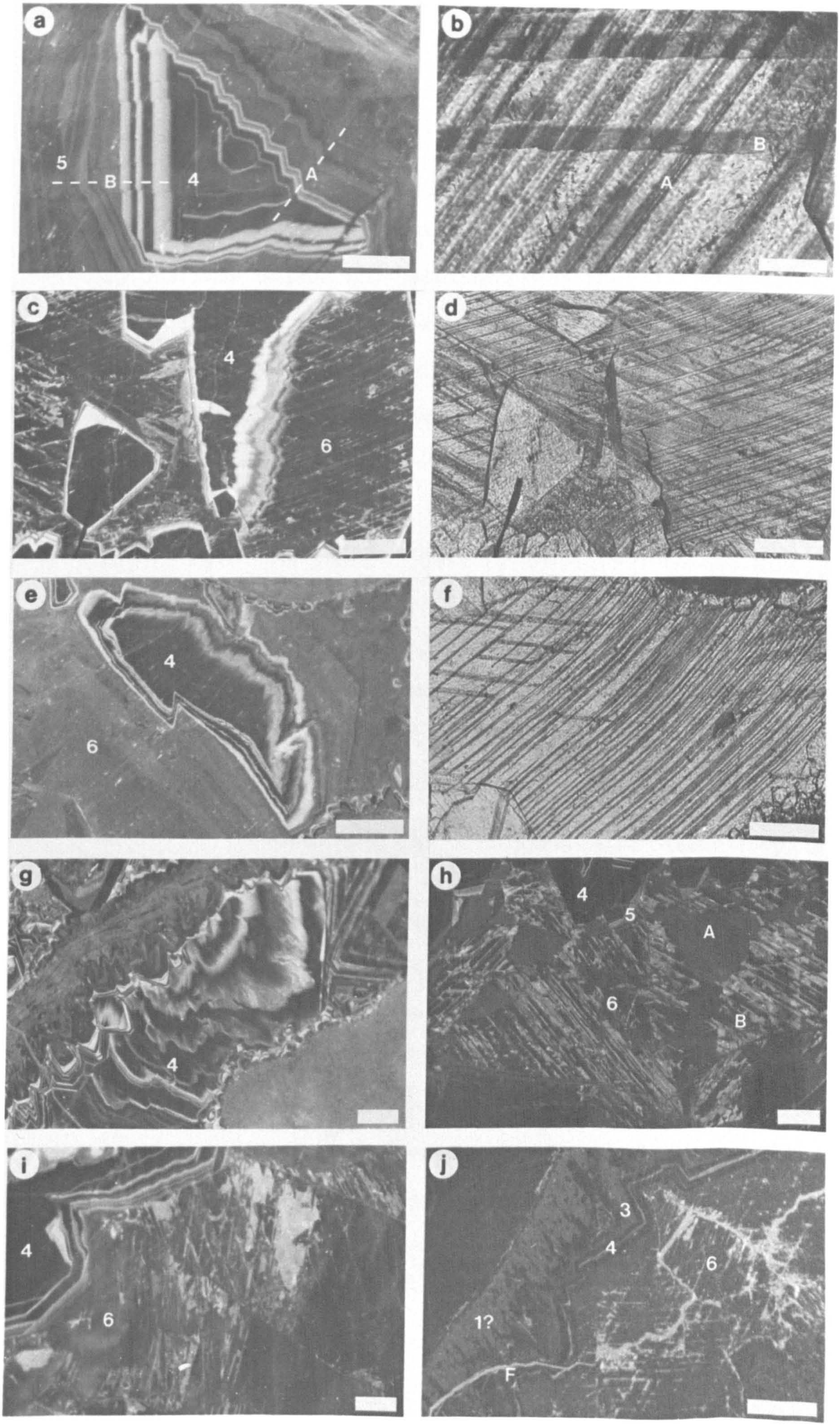
f)Transmitted light photomicrograph of the area shown in (e).Note the curved twin lamellae.Sample 18335.

g)Growth zonation 'smeared out' by deformation.The smaller crystals are unaffected.Sample 17872.

h)Zone 6 contains two types of ferroan calcite,A is less ferroan than B.B contains abundant,brightly luminescing calcite which lies parallel to twin lamellae.The brightly luminescing calcite stops abruptly at the outer margin of A although the twin lamellae can be seen to pass through A.Sample 17882.

i)Brightly luminescing calcite occurs within Zone 6 in elongate areas parallel to the trend of two sets of twin lamellae.The bright calcite stops abruptly at Zone 4,although the twin lamellae pass through it unaffected.Sample 18328.

j)Brightly luminescing calcite within Zone 6 runs parallel to the twin lamellae. It is apparently associated with similarly luminescing calcite filling a fracture (F).Sample 17872.


a
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6
1?
F

In some of the early Zone 6 calcite the CL pattern is strongly controlled by the twin lamellae. Very brightly luminescing non-ferroan calcite is concentrated in elongate areas that lie parallel to the twin lamellae (Fig. 2/33c,h,i). Although the same sets of twin lamellae run through cements of Zones 2a to 6, the brightly luminescing calcite is restricted to the more ferroan portions of Zone 6 (Fig. 2/33h). The amount of brightly luminescing calcite is very variable. Where it is abundant it is associated with numerous solid (unidentified) and fluid inclusions. In some cases the brightly luminescing calcite appears to be associated with fractures (Fig. 2/33j).

The origin of the texture described above cannot generally involve the fracture and filling of the crystals due to the restricted distribution of the phenomena within the crystals and the lack of veins indicating that fracturing of an appropriate age had occurred. Recrystallisation could be a possible explanation, but all reported occurrences of recrystallisation within twin lamellae are of the degrading type (noted above). The specificity of the phenomena suggests that it is some unique feature of the more ferroan calcite of Zone 6, perhaps its chemistry, that has resulted in an unusual, localised recrystalllisation. The connection between this phenomana and other occurrences of brightly luminescing calcite within Zone 6 (described in 2.3) is unclear. The similarity between the CL of the brightly luminescing calcite within the twin lamellae and the late Zone 6 calcite suggests that the development of these features is associated with the precipitation of late Zone 6 calcite. This cannot be confirmed without detailed chemical analysis of the two calcites. The nature of the association is unknown.

Occasionally twin lamellae have a distinctive blue luminescence. This cannot be attributed to any obvious chemical differences between the twin lamellae and the rest of the calcite. Possibly it is due to deformation of the crystal lattice within the lamellae.

The stress that caused deformation of the cement crystals occurred after the precipitation of Zone 6 since this is cut by twin lamellae. No absolute age can be attributed to the deformation. The stress probably resulted from both burial and tectonic affects. South Wales was tectonically active before, during and after the deposition of the Oolite Group (Owen, 1971).

CHAPTER THREE

SOLUTION - PRODUCTS & EVENTS

3.1 Types of solution

A variety of solution processes have operated within the Oolite Group affecting the carbonate cements and allochems. These vary considerably in their scale, mode of occurrence and result. They can be divided into the following categories:

1. removal of allochems
   a) biogenic components
   b) ooids
2. partial removal of cement crystals
   a) extracrystalline solution - solution of the free surface of a crystal
   b) intercrystalline solution - solution along crystal boundaries
   c) intracrystalline solution - solution within a crystal

These various types of solution are described in turn below.

Removal of allochems

Biogenic components

The solution of aragonite fossils is a well documented phenomena. It is one of the earliest processes affecting sub-aerially exposed Pleistocene limestones (Freidman, 1964). It is frequently recorded in ancient rocks. The outline of lost allochems may be preserved as micrite envelopes (Bathurst, 1966). The solution of aragonite by fresh waters is a result of its instability relative to low-Mg calcite in these conditions.

Of course this is not the only environment in which aragonite is lost in preference to low-Mg calcite.

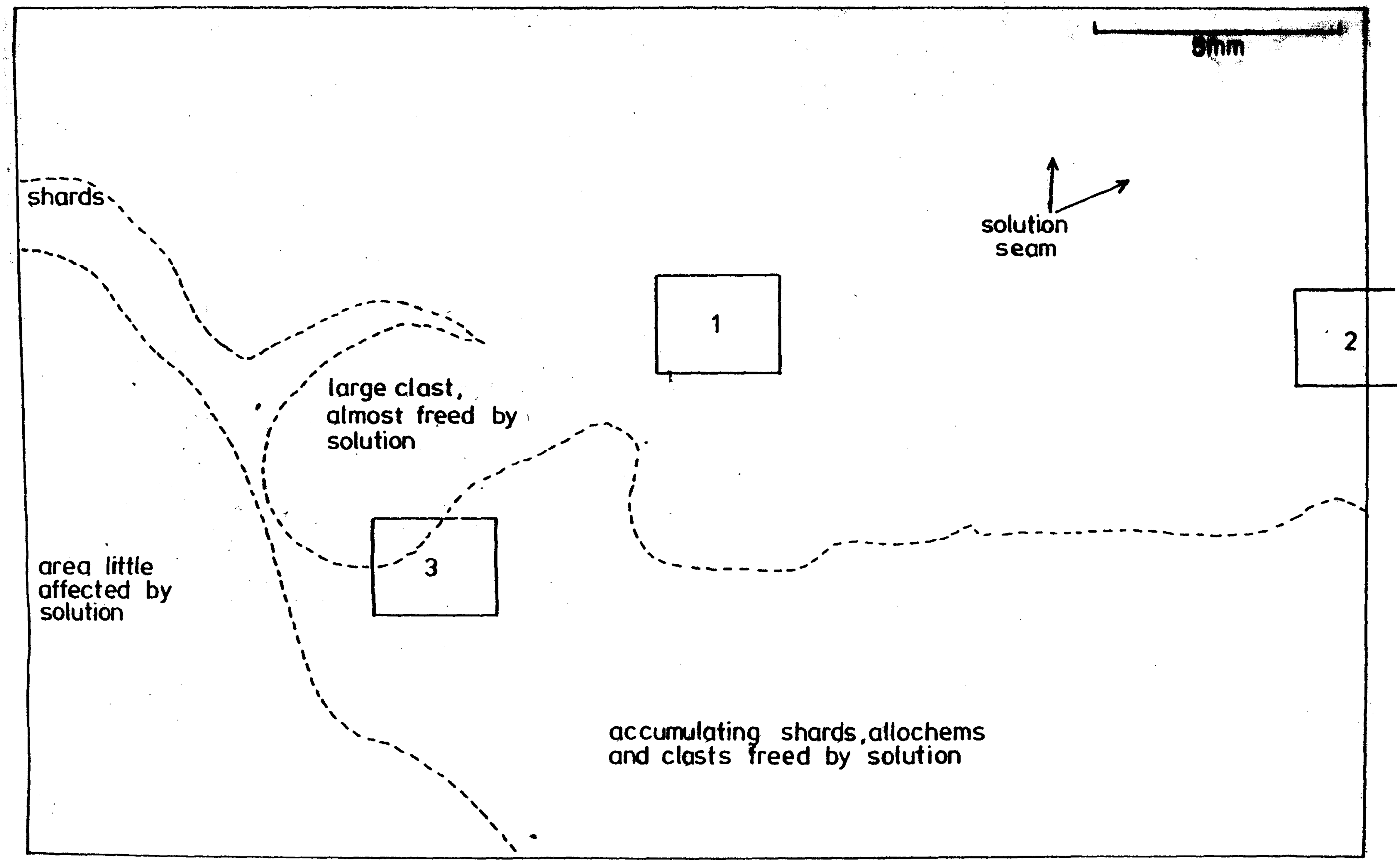
Ooid solution

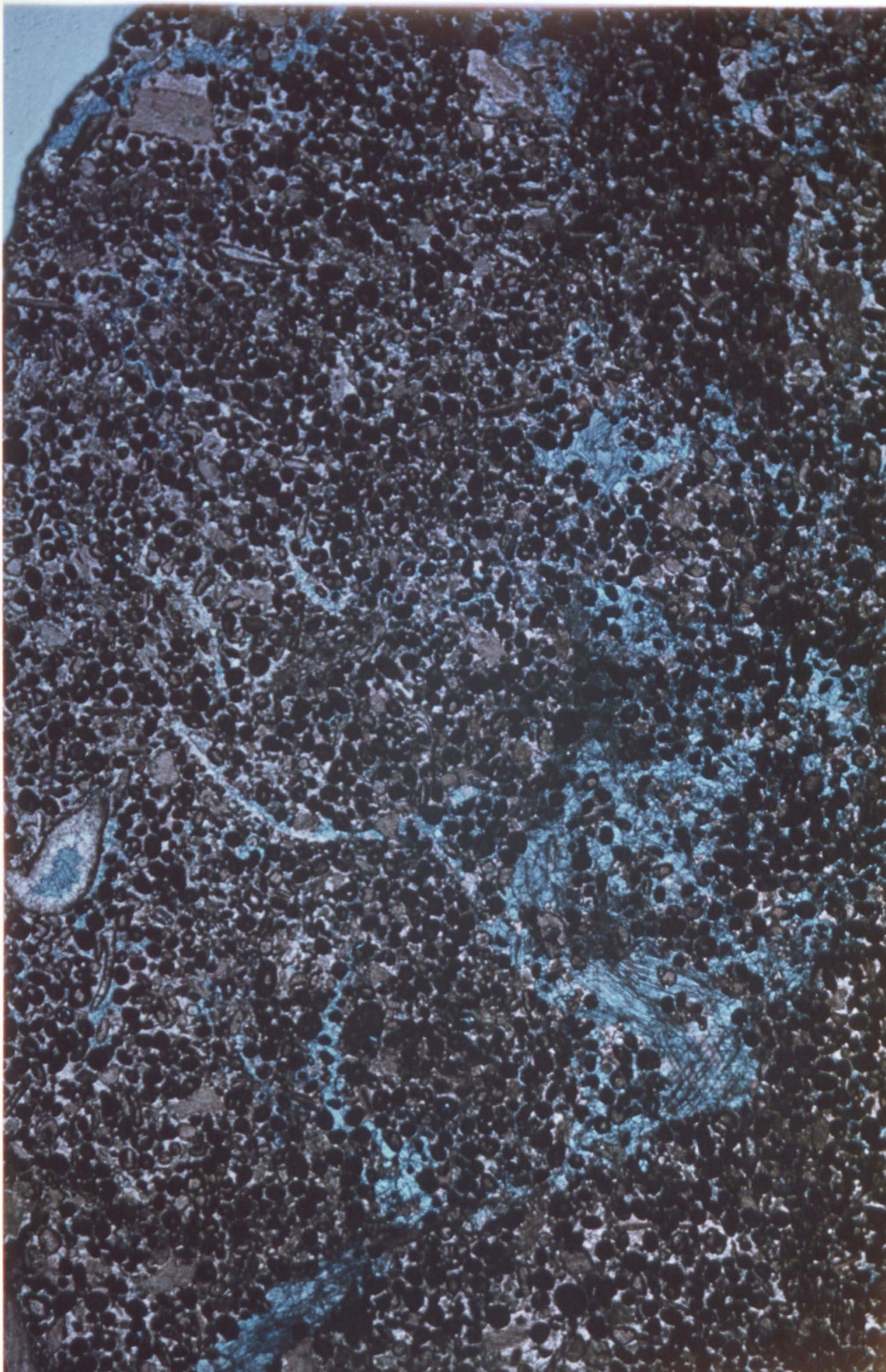
This phenomenon occurs in semi- to fully lithified rock in examples from the Oolite Group. The primary porosity, except for that in large moulds and shelter cavities, has been filled with calcite cement prior to solution. Resulting secondary porosity is filled by later cement. The solution process involves the preferential solution of ooids which results in the eventual collapse of the rock. The stages in the development of this process are described below and are illustrated in Plates 3/1, 2 and 3 and Fig. 3/1.

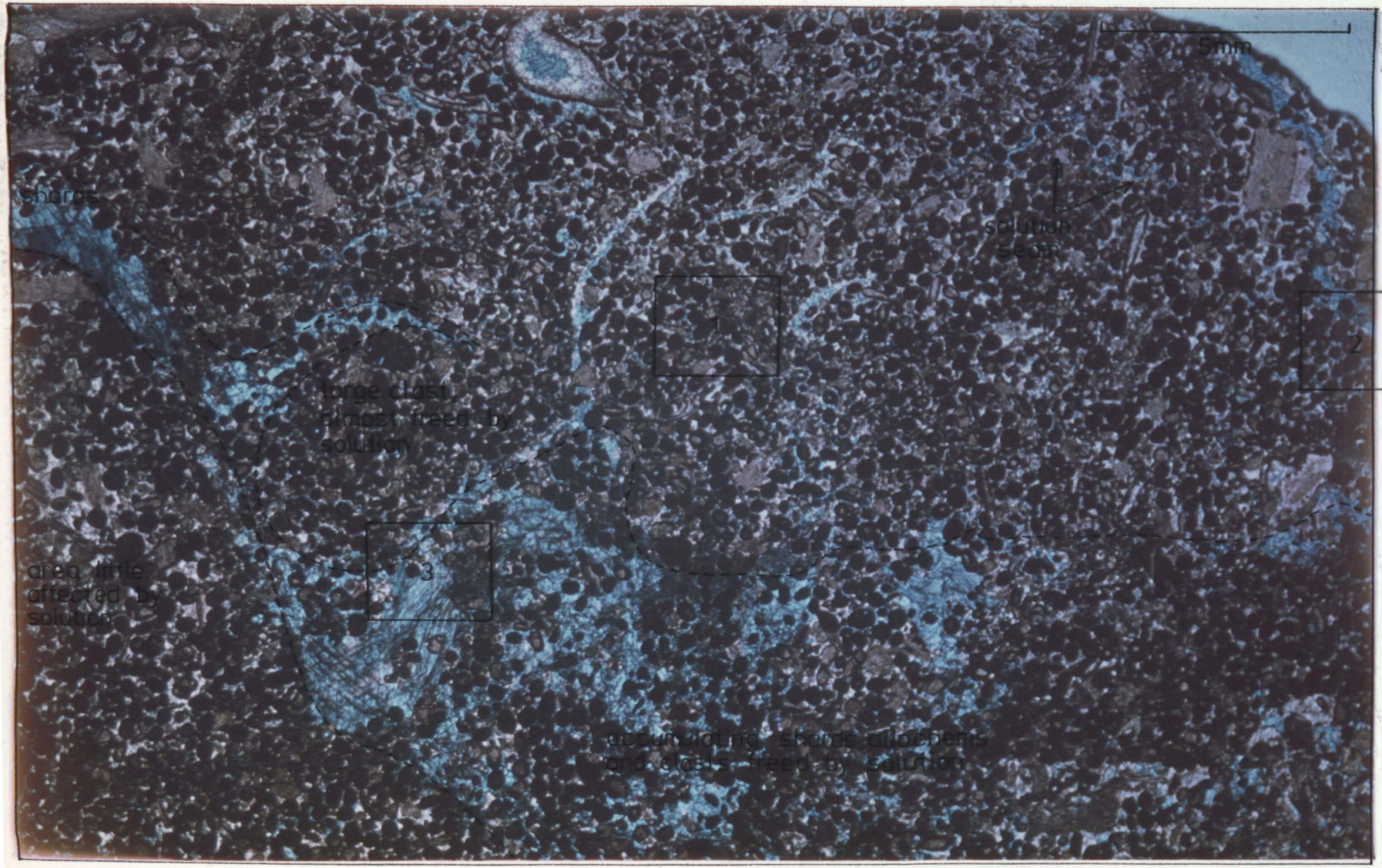
1. solution starts at the junction between ooids and cement. A solution ring is developed around ooids. In some instances the outer layer of the ooid can still be seen attached to the cement, in which case it is the ooid that has been dissolved. The result is that ooids affected like this are largely freed from their surrounding cement;
2. the cement between adjacent ooids is breached, joining the solution rings around the ooids and resulting in the formation of solution seams;
3. as solution continues the size of the solution seam increases. This may be aided by the rock beneath the seam falling away under the action of gravity. This requires that there is some sort of cavity for it to fall into. This may be a primary component of the rock, i.e. a partially filled mould or shelter cavity. Alternatively, it may be the result of earlier solution and collapse;

Plate 3/1 SOLUTION/COLLAPSE FEATURES

Transmitted light photomicrograph of a stained thin section. The area illustrated can be divided into portions much and little affected by solution. Solution seams can be seen developing in an area otherwise little affected by solution (arrows). A large 'clast' has been almost completely freed by a well developed solution seam and will eventually fall into the solution cavity which is partly filled with detatched ooids (released by solution) and scalloped cement shards. Details of the areas shown in boxes can be seen in Fig. 3/1. Sample 17849.


5mm
shards
solution seam
1
2
large clast, almost freed by solution
3
area little affected by solution
accumulating shards, allochems and clasts freed by solution

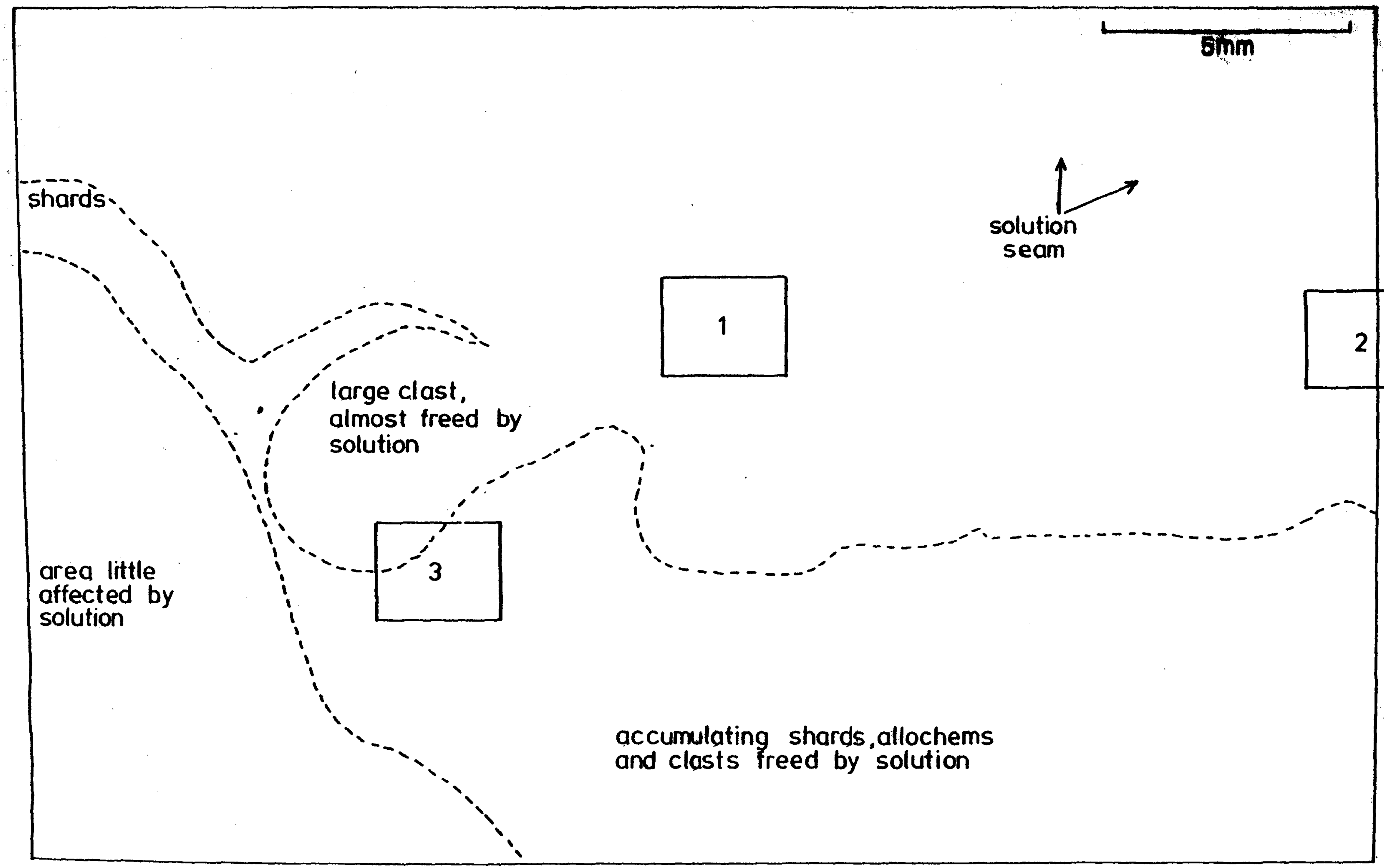


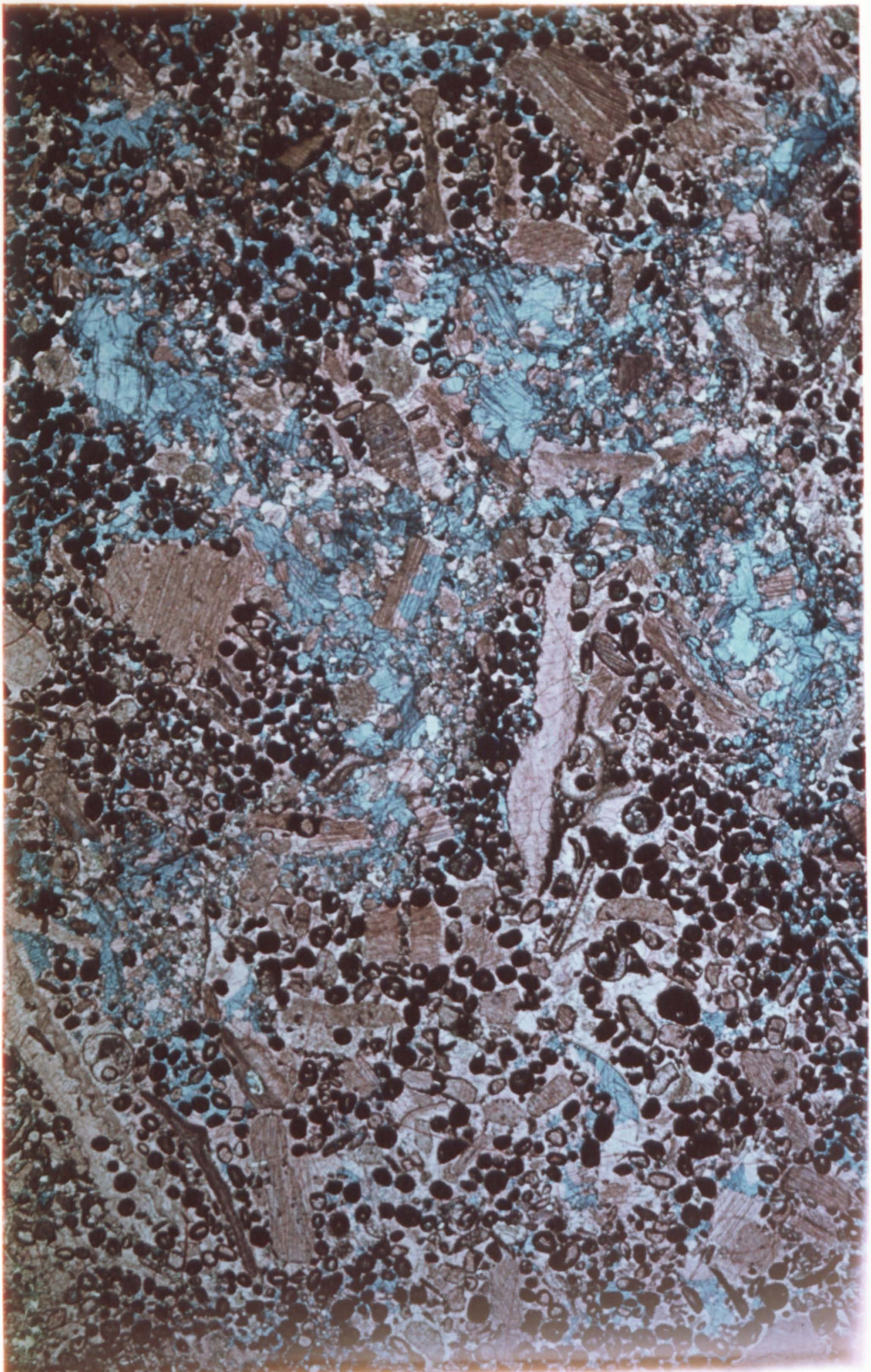


5mm
shards
solution seam
1
2
large clast almost freed by solution
3
area little affected by solution
accumulating shards allochems and clasts freed by solution

Plate 3/1 SOLUTION/COLLAPSE FEATURES

Transmitted light photomicrograph of a stained thin section. The area illustrated can be divided into portions much and little affected by solution. Solution seams can be seen developing in an area otherwise little affected by solution (arrows). A large 'clast' has been almost completely freed by a well developed solution seam and will eventually fall into the solution cavity which is partly filled with detatched ooids (released by solution) and scalloped cement shards. Details of the areas shown in boxes can be seen in Fig. 3/1. Sample 17849.


5mm
shards
solution
seam
1
2
large clast,
almost freed by
solution
3
area little
affected by
solution
accumulating shards, allochems
and clasts freed by solution



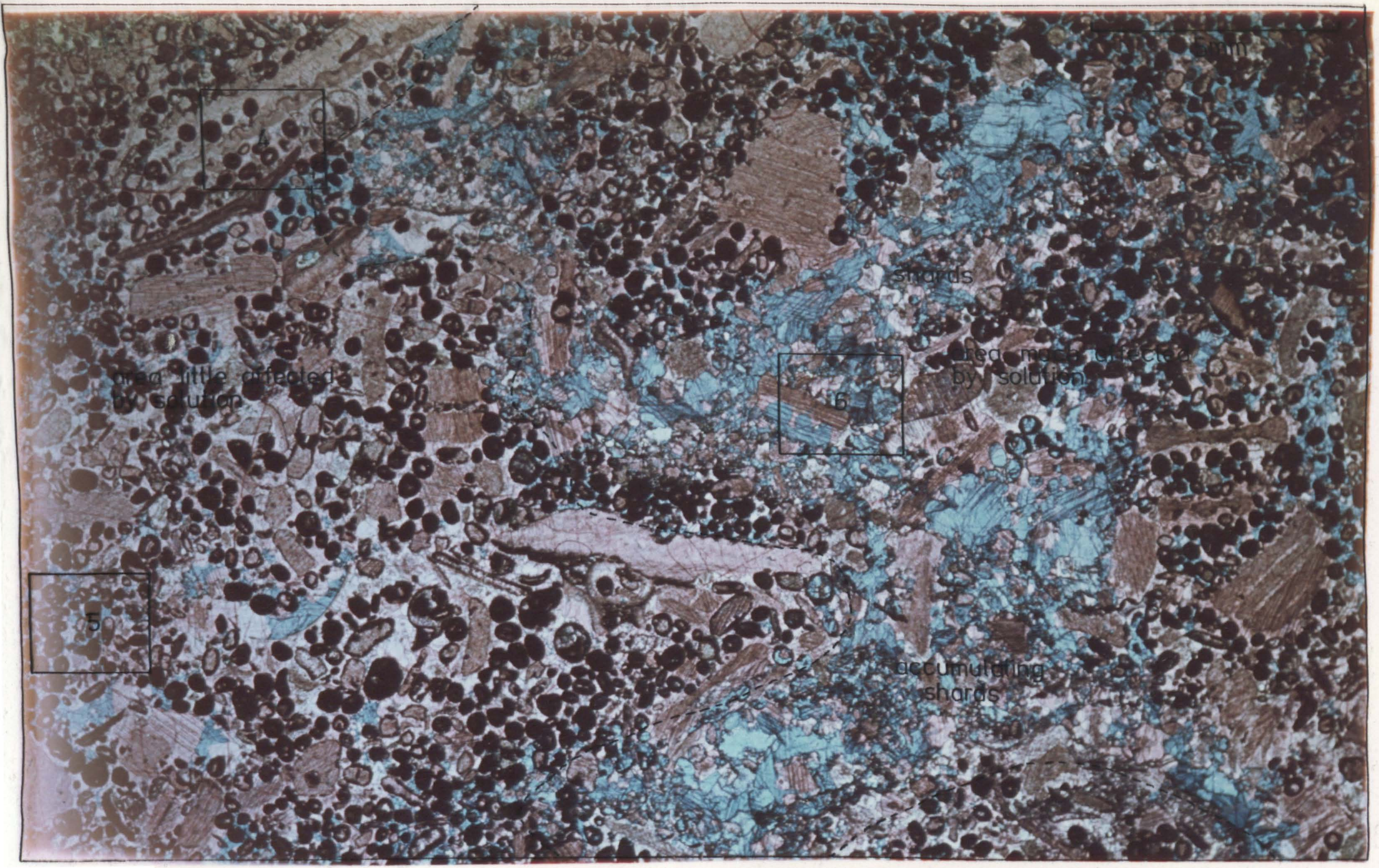
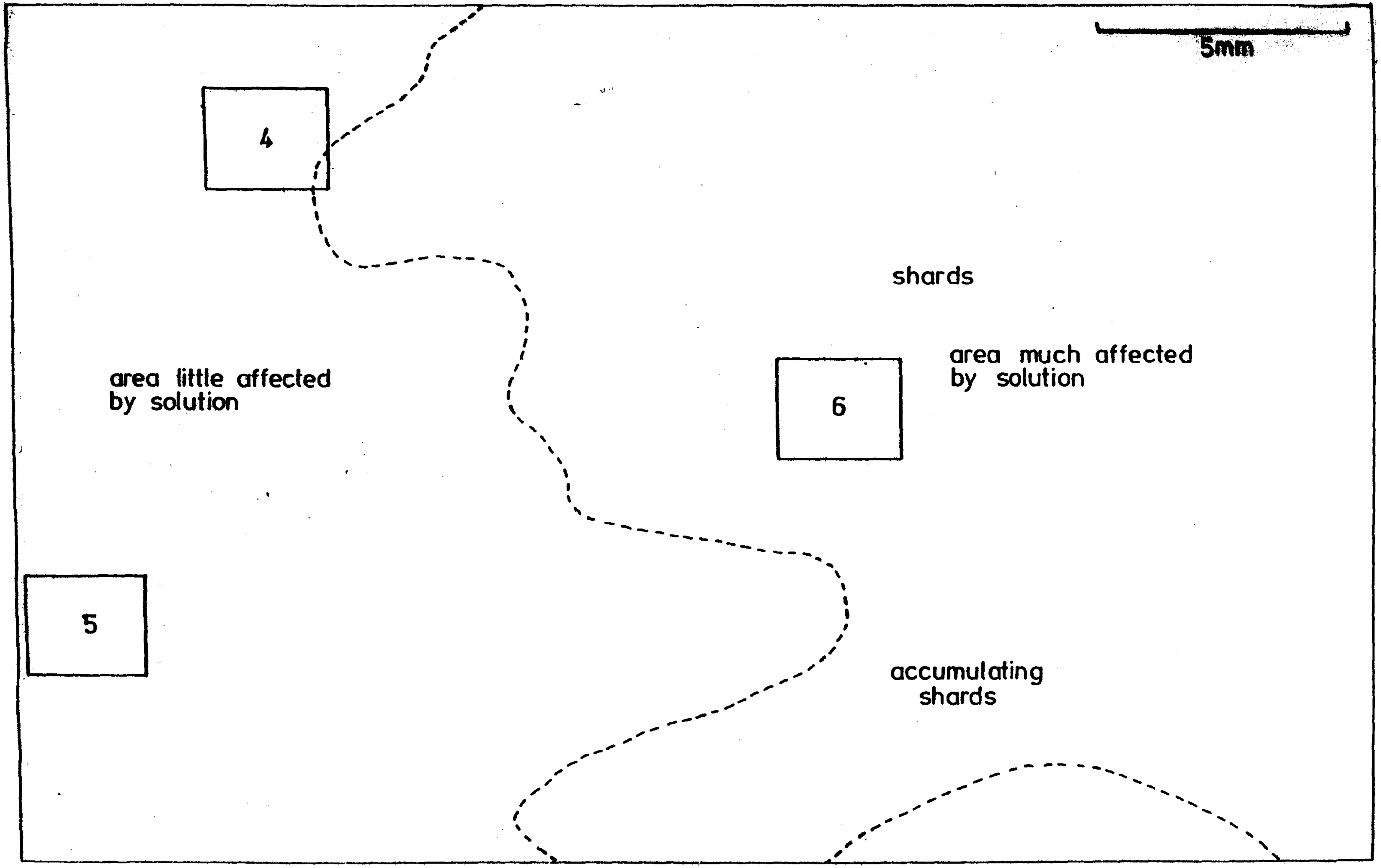
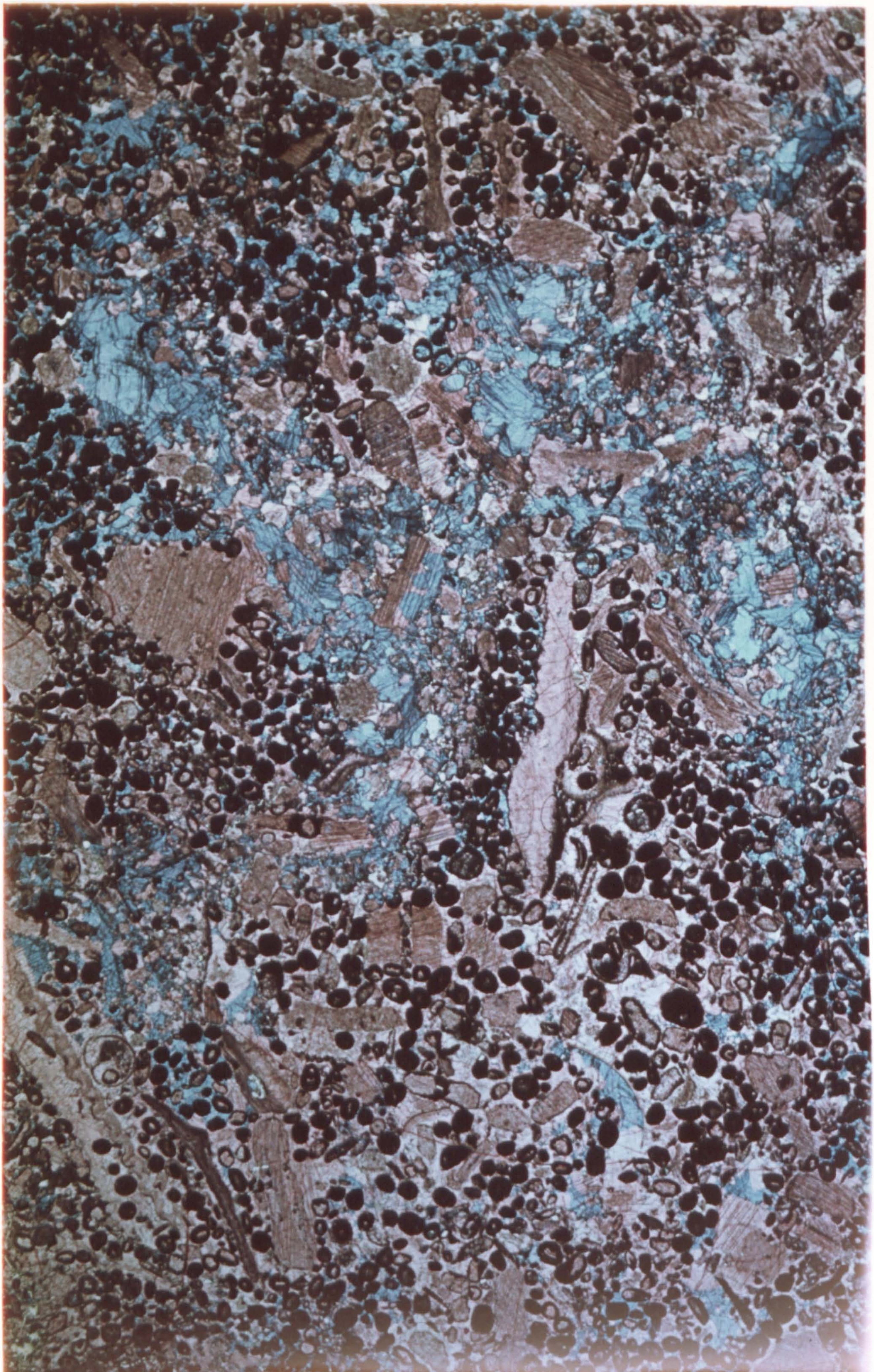

4
area little affected
by solution
5
shards
area much affected
by solution
6
accumulating
shards

Plate 3/2 SOLUTION/COLLAPSE FEATURES

Transmitted light photomicrograph of a stained thin section. The area illustrated can be divided into portions much and little affected by solution Within the area much affected by solution there are many detatched, scalloped cement shards. These are accumulating at the base of the cavity. Oomould, now filled with Zone 6 calcite(blue), can also be seen. Details of the areas shown in boxes can be seen in Fig. 3/1. Sample 17905.


5mm
4
shards
6
area much affected
by solution
area little affected
by solution
5
accumulating
shards



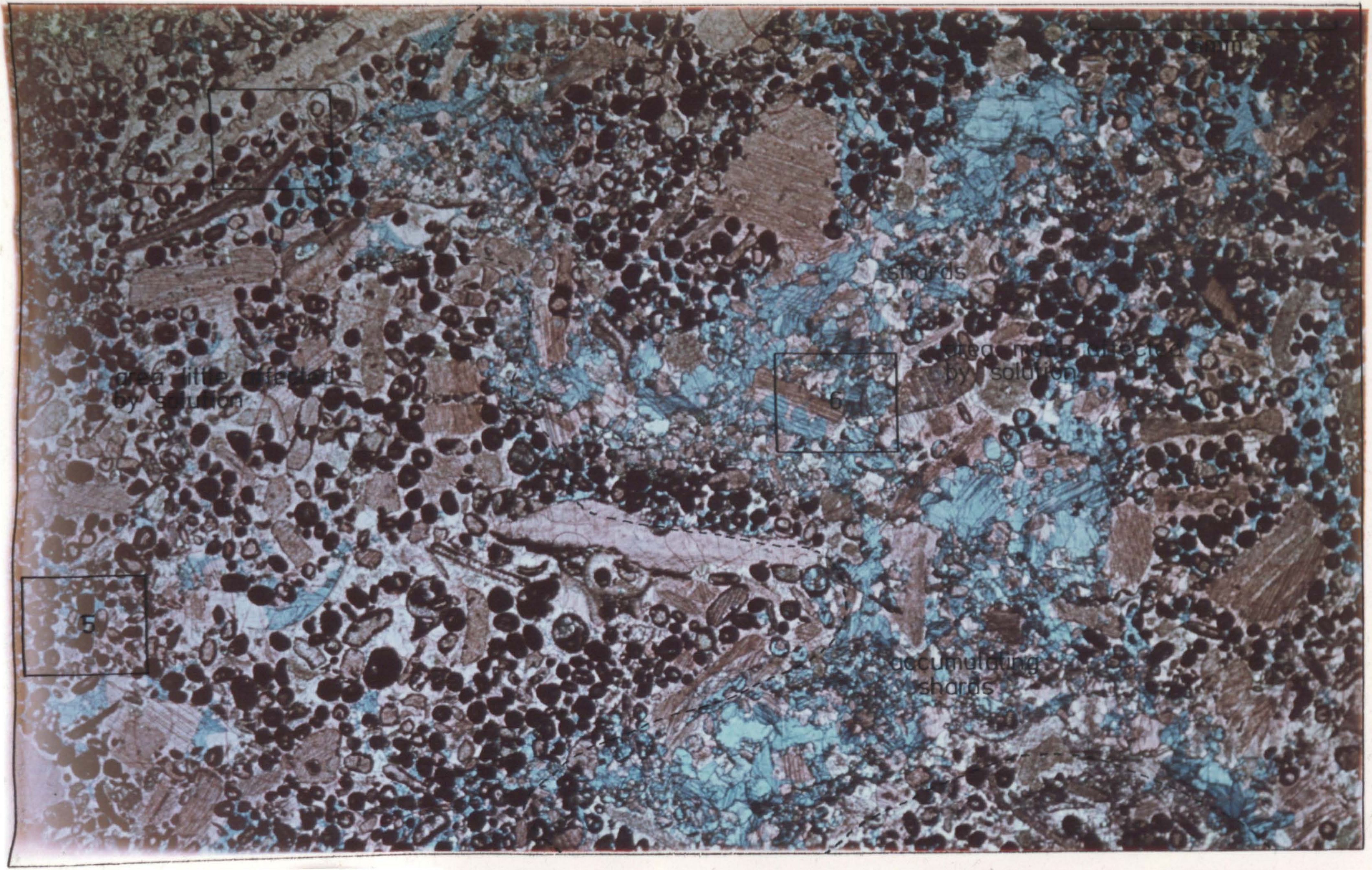

5mm
shards
area much affected
by solution
area little affected
by solution
6
5
accumulating
shards

Fig.3/1 FABRICS ASSOCIATED WITH OOID SOLUTION

Sketch enlargements of the areas outlined in boxes in Plates 3/1 and 3/2, highlighting certain fabrics associated with ooid solution.

1)An early stage in the development of a solution seam.

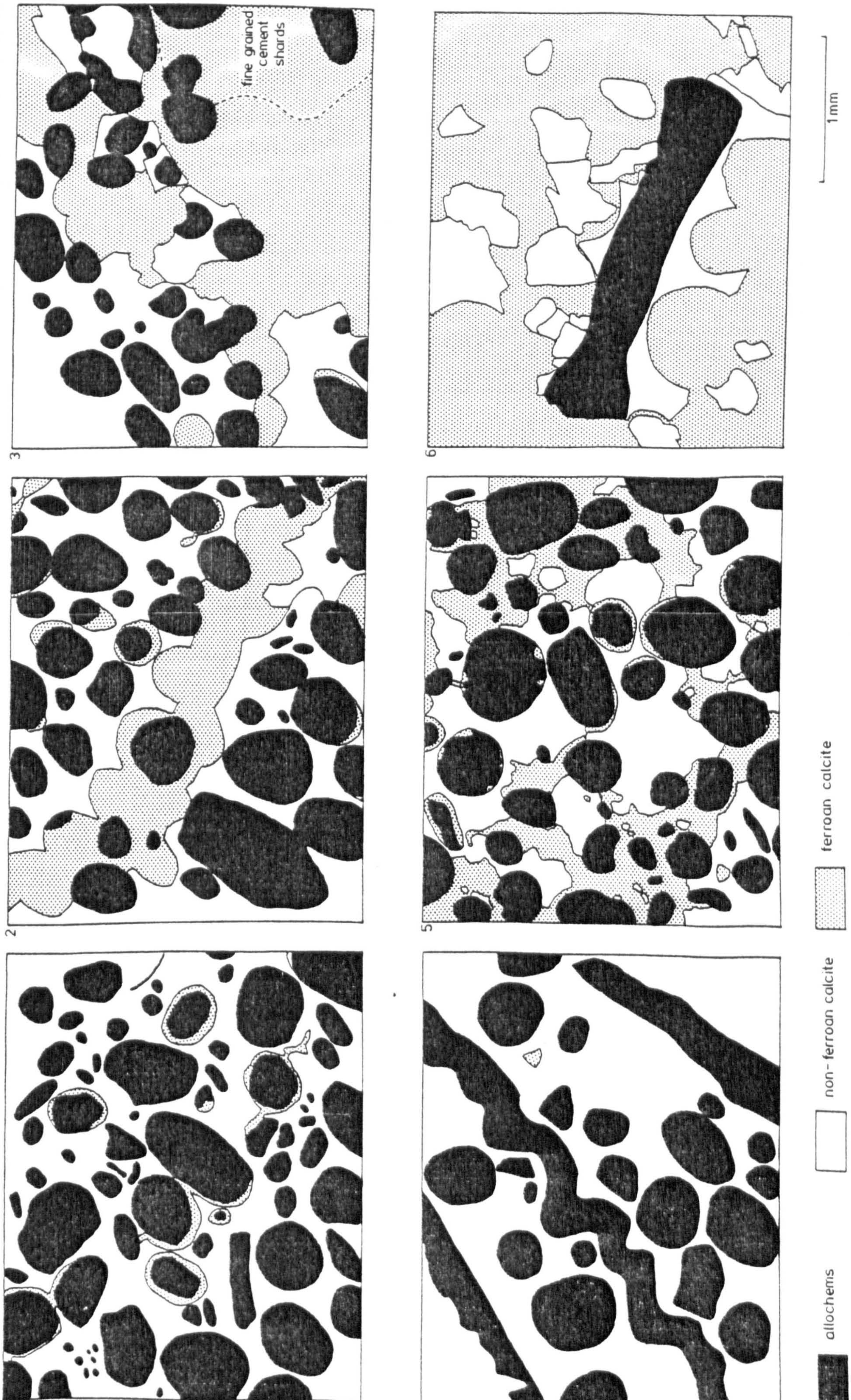
2)A well developed solution seam with allochems being released and falling out.

3)Cement shards with scalloped margins now no longer attatched to the bulk of the rock.

4)Area unaffected by solution and almost totally cemented by non-ferroan calcite.

5)An area in which numerous small solution seams have joined up resulting in the wholesale break-up of the rock.

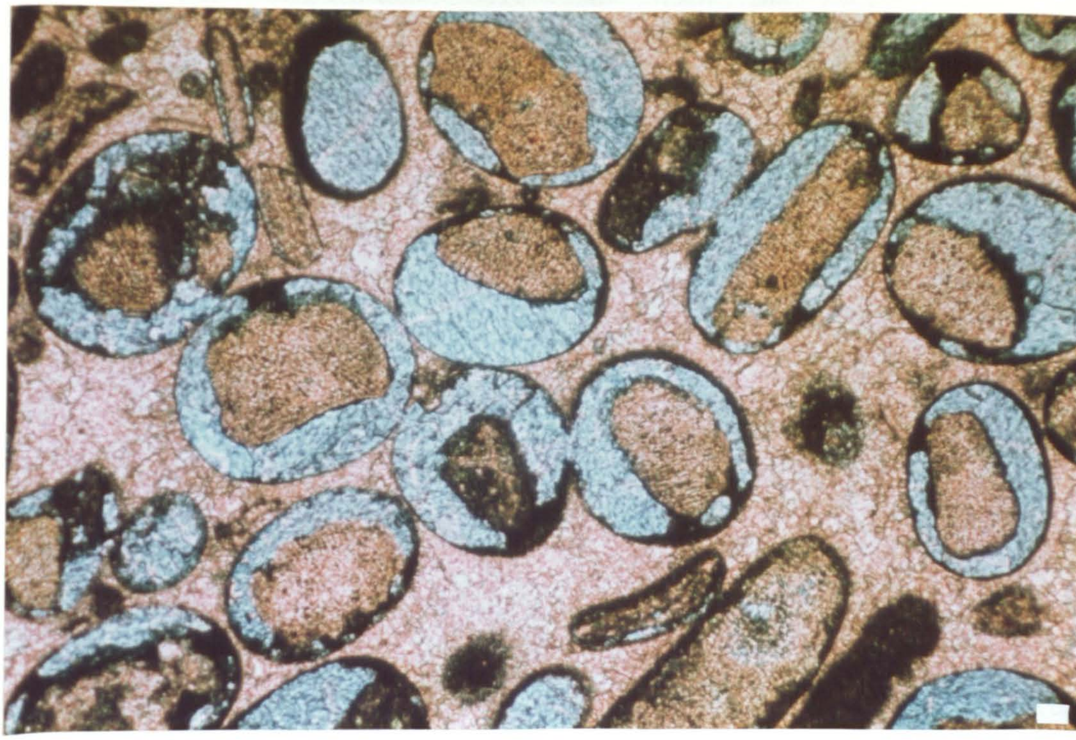
6)A large syntaxial overgrowth on an echinoderm fragment freed from the rock. Scalloped margins mark the former position of allochems.Cement shards are accumulating on top of the syntaxial overgrowth.


1
2
3
4
5
6
fine grained cement shards
1mm
allochems
non-ferroan calcite
ferroan calcite

4. ooids that were only partially dissolved in the formation of solution seams fall or are washed out of the seams when these are wide enough. This is accompanied by the break-up of the cement framework producing scalloped shards. Larger fragments are supplied by syntaxial overgrowths on echinoderm plates. These grow poikotopically, engulfing ooids. When the ooids are removed a single crystal is left whose edges are highly scalloped, the scallops representing partial oomoulds;
5. all these fragments collect at the base of cavities. Debris produced in this way is prone to pressure solution during subsequent diagenesis, whereas areas that are unaffected by this type of solution show no signs of pressure solution.
6. the process described above continues to affect the rock around cavities, solution seams and any other weaknesses. Solution seams eventually encircle and isolate clasts containing many hundreds of allochems that show no sign of solution. This results in the wholesale collapse of the rock. Pressure solution occurs along the junction of such clasts although the grains within the clasts show no signs of pressure solution.

In some instances solution seams do not develop and the ooids are dissolved in place, resulting in a network of cement containing subspherical holes (oomoulds) (Plate 3/3a). The ooids are lost either in an irregular fashion or by the removal of concentric rings from the ooid cortex. The nucleus may or may not be removed. The cement framework left after the removal of the ooids is fragile and has a tendancy to collapse (Plate 3/3b).

a



b

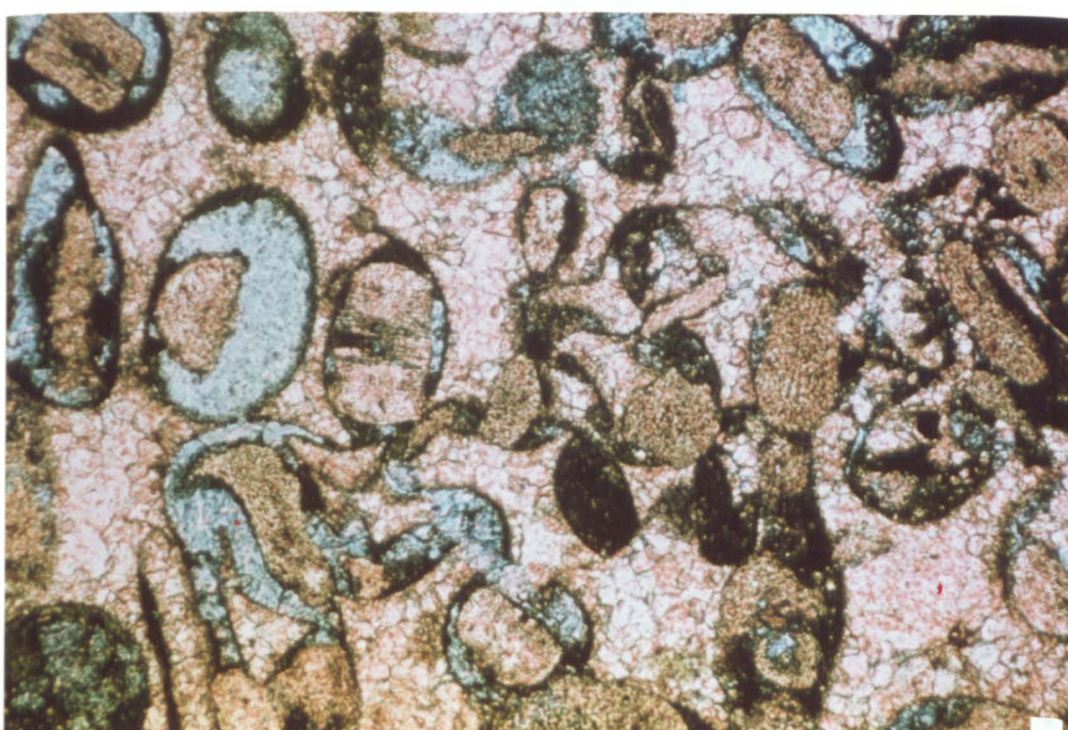


Plate 3/3 OOID SOLUTION

a) Transmitted light photomicrograph of a stained thin section. Solution has resulted in the removal of the ooid cortex leaving the nucleus, in this case echinoderm fragments. The oomoulds have been filled with Zone 6 calcite (blue). Sample 20540.

b) Transmitted light photomicrograph of a stained thin section. The cement framework left after ooid solution has collapsed forming scalloped shards. Sample 20540.

Such a process is described by Knewtson & Hubert (1969) and Conelly (1977). The collapse of the framework produces shards similar to those described in (4) above. The volume reduction associated with collapse will result in a cavity above the collapsed area.

The result of the solution-collapse process is the production of a heterogeneous rock, with unaffected areas in close association with areas showing extensive signs of solution and collapse. Large cavities may be formed in a rock that formerly had none. The longer this process continues the larger and more numerous these cavities will become.

The earliest stages of this process, which have been identified petrographically in the case of the Oolite Group, are identical to those developed experimentally by Donahue et al. (1980). They forced CO_2 charged water through fully cemented and stabilised Mississippian Ste. Genevieve Lst. simulating a depth of burial of approximately 3 km. This illustrates that selective solution does not reflect minerallogical variations between ooids and cement but rather is governed by textural criteria. Later stages of this process, as shown in the Oolite Group, were not developed in the experiments, presumably due to their short duration. It is thought that the Oolite Group solution event occurred at a fairly shallow depth since diagenetic sediment is found within solution cavities.

Many of the ooids from the Oolite Group, especially from the top of the Gilwern Oolite, are ferroan. It is impossible to identify individual areas of ferroan calcite within them. They dominantly occur at the margins of blocks in the breccia zone. They will be referred to as 'ferroan ooids'. They are thought to result from the partial leaching of ooids along the original radial fibrous crystals and the filling of the voids thus produced, with ferroan calcite.

Partial removal of cement crystals

Extracrystalline solution

This is a process that affects the free surface of crystals that project into partially filled vugs and pores. The nature of the etched surface is determined by the mechanism controlling the rate of solution (Berner, 1978). When the rate of solution is controlled by the transport of solute away from the dissolving crystal the solution surface should be smooth. When the rate of detachment of ions from the surface of the crystal controls the rate of solution selective dissolution occurs and the solution surface is irregular (Fig. 3/2a). In extreme cases the original shape of the crystal may be totally destroyed. Dissolution may result in the truncation of growth zonation.

Later calcite will grow in lattice continuity on the etched crystal surface rendering it invisible unless pre- and post-solution calcites can be distinguished in some way, i.e. by staining and/or CL. A possible lasting trace of an etched surface is a line of inclusions or impurities. Once growth recommences the crystal will strive to re-establish crystal faces. If the etched surface is irregular this will require varying growth rates in the earliest calcite precipitated. Hence, zonation above the etched surface is likely to be irregular (Fig. 3/2b).

Irregular truncation surfaces, similar to those illustrated above, are described by Meyers (1978). He illustrates 'sharp,

Fig.3/2 EXTRACRYSTALLINE, INTERCRYSTALLINE AND INTRACRYSTALLINE SOLUTION FEATURES

a) Extracrystalline solution surface developed at the outer edge of Zone 4. Sample 18353.

b) Extracrystalline solution surface (arrow) developed between Zones 4a and 4b. Note the irregular nature of the calcite immediately overlying the surface. Sample 18349.

c) Intercrystalline solution (arrows) within Zone 3. Sample 20592.

d) Brightly luminescing, zoned calcite shows intercrystalline solution. Arrows indicate where the zonation has been cut. Solution vugs are filled with non-luminescent calcite. Sample 20540.

e) Intracrystalline solution of Zone 3. The irregularly shaped, non-luminescing area within Zone 3 (arrow) is a filled solution vug which cuts across the zonation pattern. Sample 20540.

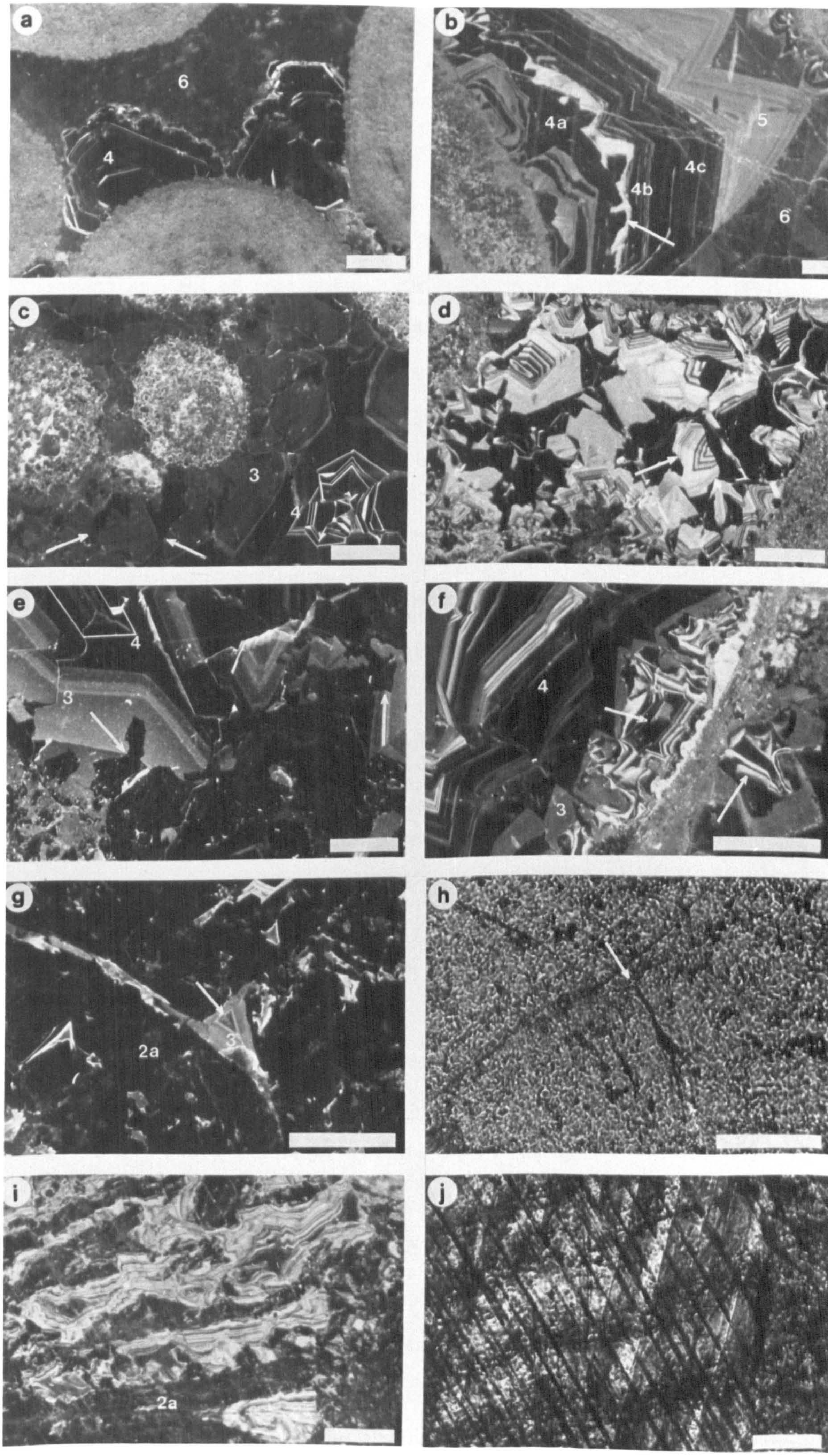
f) Intracrystalline solution of Zone 3. Zoning in the calcite filling the vugs (arrows) shows its centripetal character. Sample 17882.

g) Intracrystalline solution of Zone 2a. The vug is filled with Zone 3-like calcite that shows centripetal zoning (arrow). Sample 17882.

h) Transmitted light photomicrograph of the same area as shown in (g). A line of inclusions marks where the solution vug closed (arrow). Sample 17882.

i) Intracrystalline solution of Zone 2a. Solution vugs are filled with brightly luminescing, centipetally zoned calcite. Sample 20543.

j) Transmitted light photomicrograph of the same area as shown in (i). The areas that correspond to the fills contain fewer inclusions than true Zone 2a material. Sample 20543.


a
6
4
b
4a
5
4c
4b
6
c
3
4
d
e
4
3
f
4
3
g
2a
3
h
i
2a
j

irregular contacts' and interprets these as etched and pitted surfaces. In most of his examples a rough crystal outline is preserved (microetching), but in extreme cases the shape is completely altered. 'Type A' truncation surfaces of Fairchild (1980) are also of this sort. The surfaces he describes are very irregular with very sharp reentrants although the amount of truncation is small. Scherer (1977) illustrates multiply pitted ferroan calcite and ferroan dolomite crystals. Cross sections of these would undoubtedly have highly irregular margins.

Solution surfaces that are smooth have not been found within the Oolite Group. Smooth, rounded solution surfaces have been described by Braithwaite (1979) from tufas.

Intercrystalline solution

This type of solution occurs along the boundaries between crystals that partially or completely fill vugs and pores. It results in the production of an irregular and patchy distribution of pre-and post-solution calcite. In the Oolite Group these are distinguished using CL. Unless it is possible to see growth zonation in one or both of these calcites it may be difficult to distinguish between the calcite that has been etched and that filling the resultant solution vugs. The former should show normal growth zonation that is cut by the solution surface (Fig. 3/2c, d), while the latter should show centripetal filling of the solution vug.

The localisation of solution along crystal boundaries is a clear indication of the passage of dissolving pore waters between the crystals, even in completely filled pores. Presumably once solution has started and these pathways have become enlarged the rate of solution is increased due to the increase in the permeability and the flow rate that must result.

Intracrystalline solution

This term is used to describe solution processes occurring within individual crystals. As in previous examples these features can only be identified if pre- and post-solution calcites can be distinguished and the presence of growth zonation in these aids in interpretation. Two types of intracrystalline solution can be distinguished:

Type 1 - etching of irregular vugs within crystals

Type 2 - etching of 'regular' vugs within crystals.

These two types are described and discussed below.

Type 1 - the result of this type of solution is the formation of irregularly shaped vugs within crystals. These are filled by later calcite. The irregular outer margins of these areas are solution surfaces and they cut the growth zonation of the host crystal. These areas show no apparent connection to the free surface of the crystal that was exposed to the pore fluids at the time of solution (Fig. 3/2e). One would expect such a surface to show extra-crystalline solution features. However, it is usually impossible to identify any such surface. This may be because the area dissolved had a more soluble composition which allowed its removal whilst other zones, including that facing the pore, were not dissolved. The solution vugs are filled with later calcite that grows in lattice continuity with the host crystal and centripetally fills the vugs. The centripetal nature of the fill will only be evident if zoning can be seen within it (Fig. 3/2f).

Unfortunately in most examples from the Oolite Group this is not the case. Solution of the interior of the crystal may be very extensive and unless the centripetal nature of the fill is evident the filling calcite may be mistaken for an earlier etched calcite showing extra-crystalline solution features.

Inclusion patterns may betray the presence of filled vugs in several ways. Sometimes a line of inclusions or impurities occurs around the etched surface or along the line along which the solution vug was closed (Fig. 3/2g,h). In examples where inclusion-rich calcite has been dissolved the fills are of inclusion-poor calcite and so are visible (Fig. 3/2i, j).

It should be possible to match the calcite that fills solution vugs with part of the cement sequence and, hence, to date the age of the solution event. This often proves difficult or impossible. This may in part be due to the calcite filling solution vugs growing more quickly than that precipitated on peripheral crystal faces. Such a situation is analogous to the more rapid precipitation of calcite as syntaxial overgrowths than elsewhere and is a response to the much greater amount of growth needed to develop crystal faces. The affect of varying growth rates on the zonation pattern seen was illustrated in 2.3.

Since, in two dimensions, the solution vugs do not appear to have been connected to any crystal surface that may have been present at the time of solution there is a problem as to how dissolving fluids gained access to the interior of the crystals. It may be that the lack of connection to the surface, seen in two dimensions, is not a reflection of the situation in three dimensions. There may, in fact, have been narrow connections either to the free surface of the crystal and/or crystal boundaries along which dissolving fluids entered the crystal. This would mean that intracrystalline solution is a special case of extra- and/or intercrystalline solution.

Type 2 - this differs from Type 1 in that the shape of solution vugs is controlled by the chemistry and/or fabric of the crystals. For instance, in some cases specific growth zones would appear to have been more soluble than those around them and are removed preferentially (Fig. 3/3a). This type of solution may result in no apparent cutting of growth zones. The vugs produced will again be centripetally filled, but unless zonation can be seen this will not be apparent. Solution can proceed a considerable distance along a specific grow zone without any apparent point of entry for the dissolving fluids (Fig. 3/3b). In Fig. 3/3c the access point is from the direction of the substrate and solution has proceeded outwards until a more soluble zone was reached; it then proceeded laterally. Similar selective solution of zones is illustrated by Longman (1981) in 'cave calcite' from Pleistocene limestone from Barbados.

The shape of solution vugs may also reflect the original shape of the crystals being dissolved. For instance, fibrous crystals will dissolve to leave elongate vugs (Fig. 3/3d). Solution between fibres will have the same result. Lohmann & Meyers (1977) describe radial fibrous, inclusion-rich syntaxial overgrowths with brightly luminescing calcite

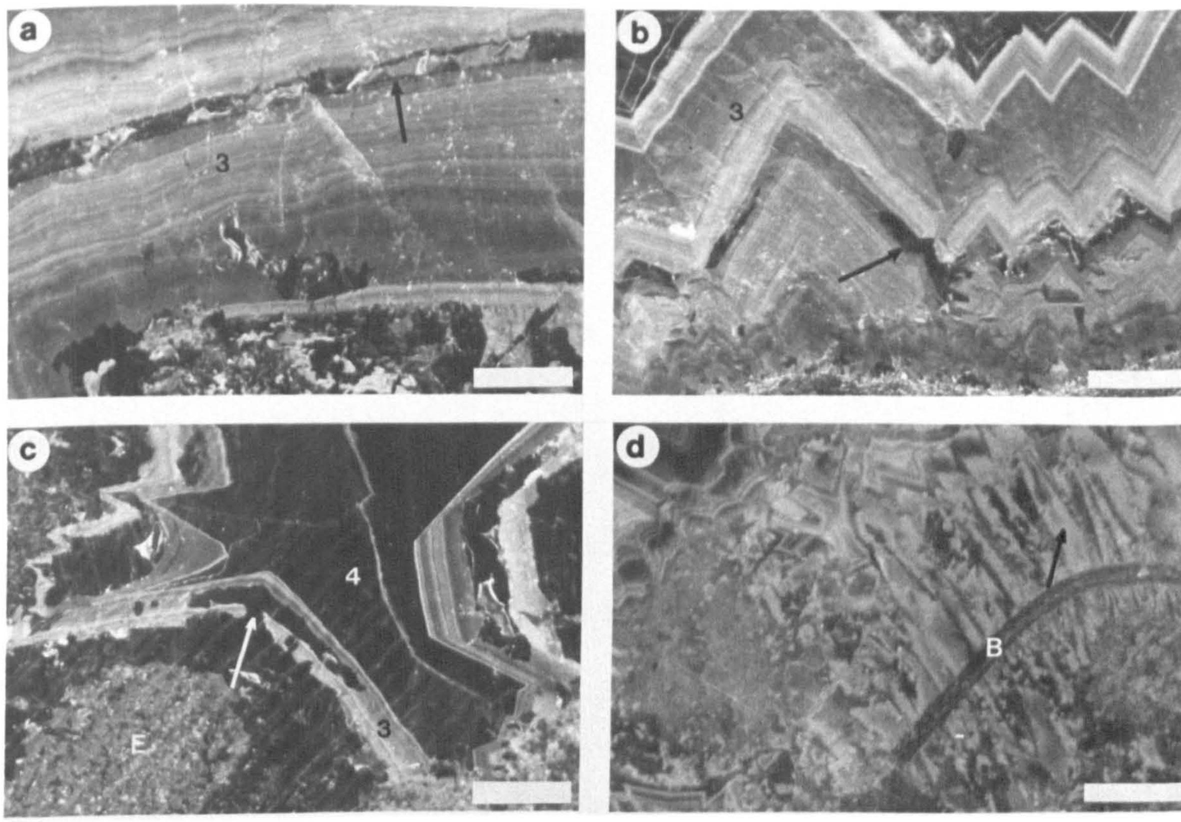
Fig.3/3 INTRACRYSTALLINE TYPE 2 SOLUTION FEATURES

a)Solution has occurred in a specific subzone within Zone 3 (arrow).Solution vugs are filled by non-luminescing,Zone 4 material.Sample 17882.

b)Solution of a specific subzone within Zone 3 has occurred (arrow).Solution extends a long distance along the subzone without any apparent point of entry for the dissolving fluids.The elongate solution vugs that result are filled with non-luminescing,Zone 4 calcite.Sample 17882.

c)In this example solution started near the echinoderm fragment (E).It proceeded outwards,cutting across the growth zonation pattern (arrow).When a more soluble zone was reached solution proceeded laterally along this zone.Sample 17882.

d)Solution has affected fibrous crystals growing on a brachiopod fragment (B). Elongate solution vugs resulted that have now been filled with brightly luminescing calcite (arrow).Sample 17825.


a
3
b
3
c
4
3
E
d
B

filling either inter-fiber areas or solution enlarged pores between fibres. The luminescent fabric resulting mimicked the fibrous nature of the precursor. Such areas passed laterally into areas with 'blotchy' luminescence.

3.2 Solution events within the Oolite Group

A number of solution events have been identified within the Oolite Group. These show a variety of the solution features outlined earlier in this chapter. The various solution events discussed below and summarised in Fig. 3/4 are only seen in rocks showing the normal cement sequence (Zones 2a, 3, 4, 5, 6). Rocks in which Zone 1 is developed will be commented on at the end of this chapter.

Solution event 1

The earliest solution event recorded in the Oolite Group involves the removal of what are presumed to be aragonite allochems (bivalves and gastropods). This occurred during 'early' diagenesis, between the precipitation of 'early' marine cements (if present) and Zone 2a. The latter can be seen growing into moulds produced by this solution event (Fig. 3/5c, d). There is abundant evidence of subaerial exposure of the Oolite Group during its sedimentation and, hence, ample chance for fresh water to have been introduced into the Oolite Group. It is likely that the solution of aragonite allochems occurred on several occasions during sedimentation. It has already been demonstrated that Zone 2a does not represent a single precipitation event.

Solution event 2

This solution event affects Zone 2a cements. The patchy nature of the CL of this zone was briefly described in 2.1. This is

DEPOSITION	CEMENTATION	SOLUTION	TYPE OF SOLUTION FEATURES
sedimentation of the Oolite Group	marine, fibrous cement		
	Zones 1&2a	Event 1 Event 2	loss of aragonite allochems intracrystalline Types 1 & 2a,(b?)
	'early' Zone 2b		
	Zone 3		
	Zone 4a		
exposure of top of the Oolite Group		Event 3	extracrystalline, intercrystalline, intracrystalline Types 1 & 2a
sedimentation of the Llanelly Fm. early diagenesis of the Llanelly Fm.			
+	?		
	'late' Zone 4b-d	Event 4	ooid solution, extracrystalline, intracrystalline Types 1&(2a?)
	Zone 5		
	Zone 6		

TIME

Fig.3/4 SOLUTION EVENTS AFFECTING THE OOLITE GROUP

Table showing the nature of solution events affecting the Oolite Group and their timing relative to the precipitation of cement Zones 1 - 6. The timing of deposition relative to the precipitation of Zones 1 - 6 is also shown. The absolute timing of the diagenetic events shown is not known. The most probable period over which an event occurred is shown by a black bar. The maximum possible period over which an event occurred is shown by a dotted, open bar.

Fig.3/5 SOLUTION EVENTS 1 AND 2

a)Intracrystalline Type 1 solution within Zone 2a.Solution vugs are filled with centripetally zoned,brightly luminescing calcite.Sample 17905.

b)The complex luminescence pattern of Zone 2a and perhaps Zone 3 is due to the development of two sets of Type 1 intracrystalline solution vugs.The earlier set is filled with brightly luminescing calcite that is more brilliant at its outer edge.These are cut by a set of vugs filled with non-luminescing calcite (arrow).Sample 17862.

c)Zone 2a shows elongate,brightly luminescing areas within it - Type 2 intra-crystalline solution vugs.Note that they do not originate at the junction between Zone 2a and the substrate.Sample 17825.

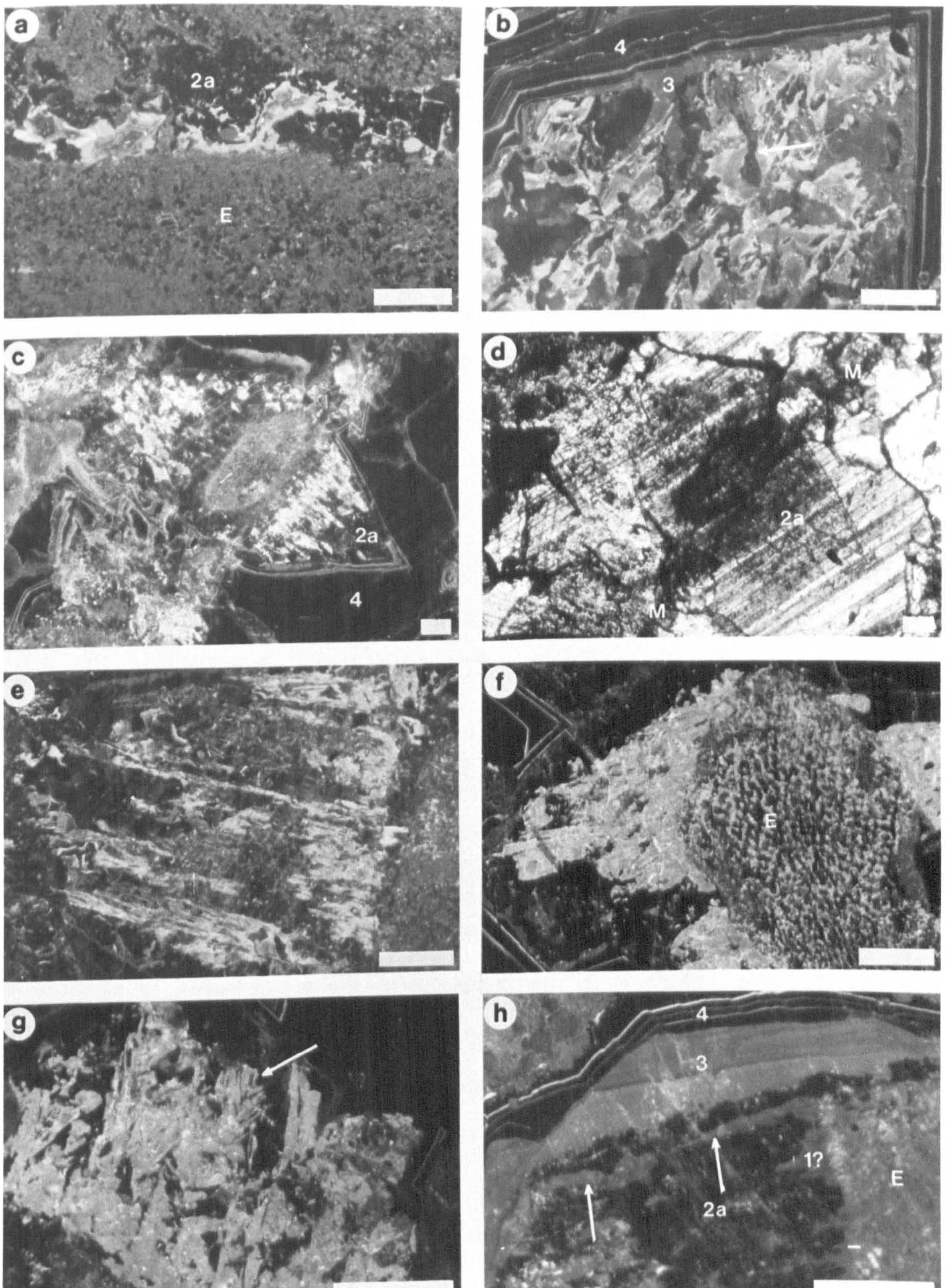
d)Transmitted light photomicrograph of the area shown in (c).Zone 2a calcite can be seen growing across a micrite envelope (M),into an area left by the solution of a bivalve(?) shell.Sample 17825.

e)Abundant,brightly luminescing,elongate areas extending across the whole of Zone 2a.Sample 12303.

f)Brightly luminescing calcite forms a syntaxial overgrowth on echinoderm fragment (E).It forms crude spires.It seems to be made up of a number of fibrous bundles that probably reflect its original fabric.Sample 17889.

g)Brightly luminescing calcite showing a relic fibrous habit (arrow).Sample 17905.

h)Elongate areas of ferroan calcite within Zone 2a (arrow).This may result from the etching of Zone 1 or the filling of elongate solution vugs within Zone 2a with Zone 3 calcite.Sample 17872.



a
2a
E
b
4
3
c
2a
4
d
M
2a
M
e
f
E
g
h
4
3
1?
2a
E

thought to result from the development of intracrystalline Type 1 and Type 2 solution features. The variability in the development of these features was commented on in 2.3.

The patches of brightly luminescing calcite that occur within Zone 2a are more brilliant at their outer margin (Fig. 3/5a, b). Other than this there is rarely any other evidence to corroberate the centripetal filling of these areas. Occasionally more abundant zonation within the brightly luminescing calcite confirms the centripetal growth of calcite in these areas (Fig. 3/5a) and, by analogy, other brightly luminescing areas are thought to have a similar origin. The bright calcite filling the solution vugs cannot be correlated with any zone within the cement sequence outlined in 2.3. An exception is the well zoned, brightly luminescing calcite illustrated in Fig. 3/2i. This may be analogous to brightly luminescing calcite from samples nearby (Fig. 3/2d). Unfortunately the position of this cement in the zonal sequence is unclear. It probably pre-dates Zone 3. The absence of these brightly luminescing areas in cement younger than Zone 2a suggests that this solution event occurred shortly after Zone 2a precipitation. It is probable that solution occurred on more than one occasion since the Zone 2a cements do not represent a single precipitation event. It is probable that solution events 1 and 2 overlap and may in fact be equivalent.

Type 2 intracrystalline solution features consist of elongate areas whose axes lie parallel to the maximum growth direction of the Zone 2a syntaxial overgrowths (Fig. 3/5c, e). The central elongate areas tend to be the longest, mimicking the development of crystal faces. In some cases they may extend the whole width of Zone 2a. The elongate areas tend to be most dense nearest to the substrate, although they do not necessarily originate from it. Similarly luminescing areas occur as Type 1 features in the same or nearby syntaxial overgrowths (Fig. 3/5a, b). A similarly luminescing calcite is also seen partly filling the stereome of echinoderm remains.

Rarely, brightly luminescing areas show more structure (Fig. 3/5f, g). These are reminiscent of the CL fabrics described by Lohmann & Meyers (1977). The lack of zonation means that it is impossible to be sure about the origin of these fabrics. There are three possibilities:

1. the brightly luminescing areas are the fills of cavities left by former unstable, fibrous cements that have been dissolved out;
2. the brightly luminescing calcite is filling inter-fiber areas;
3. the brightly luminescing calcite is a primary or a neomorphosed primary cement.

Type 2 features described above are also thought to reflect a former fibrous habit.

As well as brightly luminescing calcite, patches of dull luminescing ferroan calcite are also found in Zone 2a cements. These may be the fills of vugs produced by the same or another solution event as the vugs filled with the brightly luminescing calcite. It is impossible to tell from the evidence available. Centripetal zoning can be seen in some of these areas (Fig. 3/2g). The appearance of this dull calcite suggests that it is of Zone 3 age. As well as the occurrence described above, dull luminescing ferroan calcite also occurs filling elongate areas within Zone 2a, in a similar way to the Type 2 solution features filled with brightly luminescing calcite (Fig. 3/5h). The dull calcite is most abundant between the substrate and the syntaxial overgrowth. In stained thin sections this has been described as 'poorly defined Zone 1' (Fig. 2/13c). Where this feature occurs the lack of zonation within the dull luminescing calcite means that it is impossible to tell whether it is a solution feature. The following two possibilities exist for its origin:

1. Zone 3 cálcite is filling solution vugs in Zone 2a
2. the dull luminescing, ferroan calcite is Zone 1 material that has been etched and overlain by Zone 2a calcite.

The long, thin nature of the ferroan calcite areas suggests that (1) is the most likely origin, since it is unlikely that the pinnacles of ferroan calcite that would have resulted if (2) were true, could be self-supporting.

Solution Event 3

Areas that are dominantly non-luminescing occur within Zones 2a and 3, cutting across the zonation pattern and earlier solution features (Fig. 3/2e, 3/5b). Only rarely do they show any zonation themselves. When they do it consists of brightly luminescing, hairline subzones (Fig. 3/2f). Where present these demonstrate centripetal filling of these areas. This solution event obviously post-dates Zone 3 precipitation and the similarity of the CL of the fills to Zone 4 calcite suggests that the fills are of Zone 4 age. Rarely the vugs are not completely filled with Zone 4 calcite and the final fill is of Zone 5 age (Fig. 3/6a). The unconformity that exists between Zones 4a and 4b may, in some cases, be construed to be an extracrystalline solution surface (Fig. 3/2b). The solution event responsible for this surface is likely to be the same as that responsible for the

Fig.3/6 SOLUTION EVENTS 3 AND 4 AND SOLUTION WITHIN DIAGENETIC AREA 1

a)Intracrystalline Type 1 solution vug within Zone 3 filled with Zone 4 and 5 calcite.Sample 20596.

b)Zone 5 growing on the surface of a partial oomould (arrow) developed during Solution Event 4.Sample 17899.

c)Extracrystalline solution surface developed at the outer edge of Zone 4 and overlain by Zone 5.Note the truncation of the zonation pattern (arrow). Sample 17889.

d)Intracrystalline Type 1 solution vug within Zone 4 and filled by Zone 5 calcite.Sample 17883.

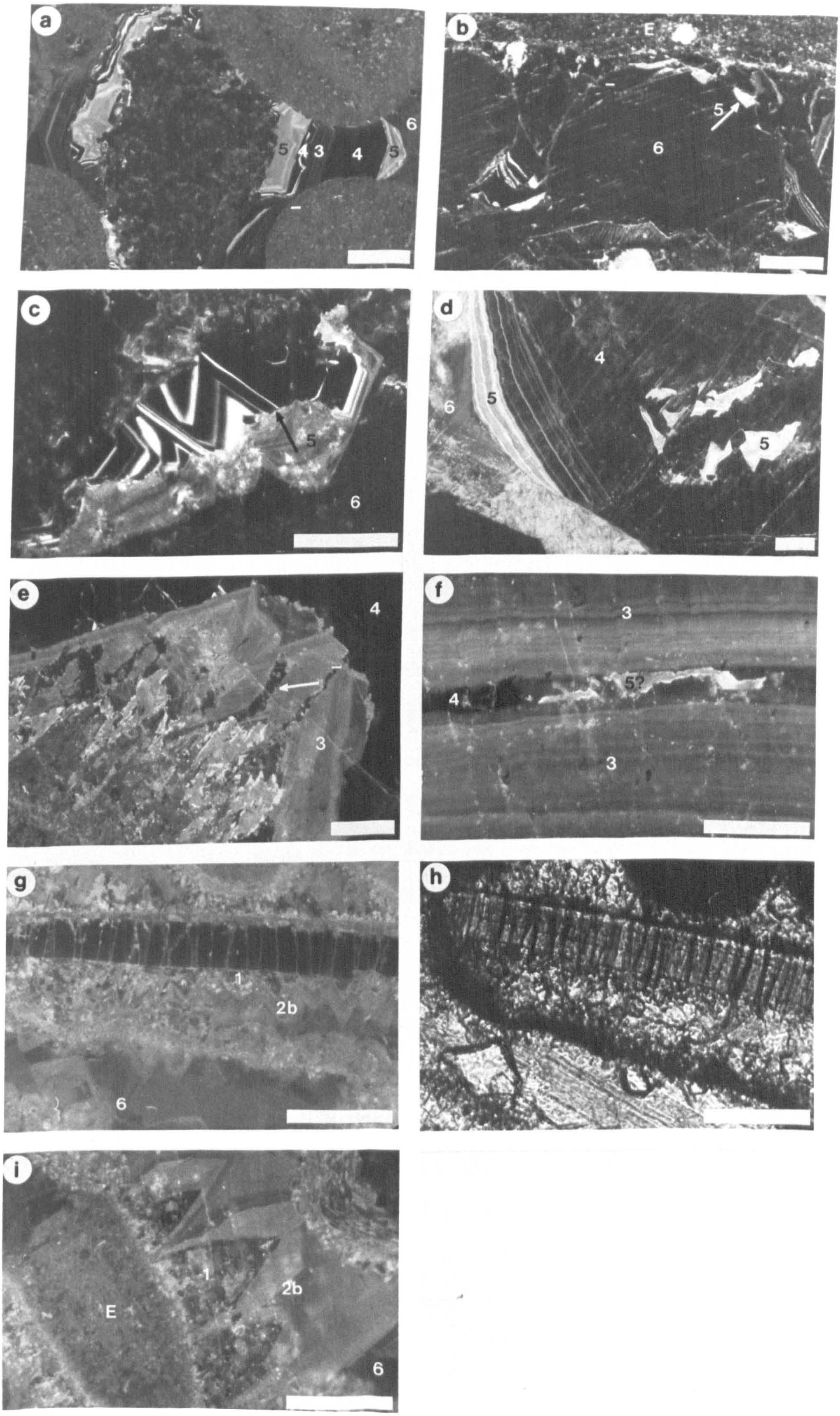
e)Two ages of solution vugs affecting Zone 3.The earlier is filled with non-luminescing calcite and cuts the growth zonation pattern (arrow).These are cut by a later set of vugs filled with brightly luminescing calcite,perhaps Zone 5.Sample 17880.

f)Intracrystalline Type 2 solution vug within Zone 3.Brightly luminescing calcite (Zone 5?) fills vugs as well as non-luminescent calcite that is of Zone 4 age.Sample 17882.

g)Mould of a former aragonite fossil filled by Zone 1,2b and 6 calcites.Sample 18313.

h)Transmitted light photomicrograph of the area shown in (g).Sample 18313.

i)Zone 1 showing patchy luminescence that may be the result of solution processes.Sample 18313.


a
5 4 3 4 5
6
b
E
5
6
c
5
6
d
6
5
4
5
e
4
3
f
3
4
5?
3
g
1
2b
6
h
i
1
2b
E
6

development of the features described above. It has previously been suggested that this solution event corresponds to the period of exposure that occurred between Oolite Group and Llanelly Fm. sedimentation; at which time fresh waters would have been introduced into the Oolite Group.

Solution at this time mainly resulted in the development of Type 1 and Type 2 intracrystalline solution features. The latter is represented by the removal of specific subzones from Zone 3 (Fig. 3/3a, b, c). Cases of extracrystalline, intercrystalline and ooid solution are rare but do occur.

Solution Event 4

Ooid solution is the dominant process during this solution event, with the resulting wholesale collapse of the rock. The growth of Zone 5 cement on the surface of oomoulds (Fig. 3/6b) demonstrates that this solution event occurred between the precipitation of Zone 4 and Zone 5 calcite. Extracrystalline solution features of the same age are found (Fig. 3/2a, 6c). Areas within crystals which have a CL similar to Zone 5 cement can be found (Fig. 3/6d), suggesting solution of earlier calcite, dominantly Zones 2a and 3, also occurred at this time, with the development of intracrystalline Type 1 and Type 2 features. In places these cut intracrystalline solution features developed during solution event 3 (Fig. 3/6e). Further solution of the subzone that was partially removed from Zone 3 cement during solution event 3 may have occurred (Fig. 3/6f). Alternatively, Zone 5, in this case, may be filling vugs that were formed during solution event 3 but failed to be filled by Zone 4 cement.

The absolute age of this solution event is not known as it is not possible to accurately date Zone 4 and 5 cements. It certainly post-dates the sedimentation and early diagenesis of the Llanelly Fm. The Oolite Group could not have been buried at any great depth during this solution event as diagenetic sediment overlies Zone 5 cement.

Rocks containing Zone 1 cement show solution event 1. It is manifested in the same way as rocks containing the normal cement sequence, i.e. by the removal of aragonite allochems. This event pre-dates the precipitation of Zone 1 calcite (Fig. 3/6g, h).

Zone 1 cement often has a blotchy appearance (Fig. 3/6i). The irregular areas within Zone 1 have a variety of luminescent tones. No evidence exists to suggest that these are centripetally filled areas, so their origin remains unclear. One possible origin is that they are the fills of Type 1 intracrystalline solution vugs.

CHAPTER FOUR

DOLOMITE AND POST-DOLOMITE CALCITES

4.1 Dolomite

4.2 Post-dolomite calcite

The dolomites in the study area have not been considered in detail as the aim of this project was to look at the cements of the Oolite Group. The dolomite, being dominantly replacive, has destroyed these cements. Primary, void filling dolomite is occasionally found partly and completely filling veins and large primary pores. The post-dolomite calcites found within the dolomitised area are considered in more detail. As a primary precipitate it is possible that equivalent calcite was precipitated as a cement in the undolomitised portion of the Oolite Group.

4.1 Dolomite

It has been mentioned previously that much of the outcrop east of Clydach is dolomitised, chiefly the beds below the Gilwern Oolite, which is also patchily dolomitised. The distribution of dolomite is shown in Fig. 2/28b. The dolomite that replaces the oolite members is coarse grained (0.2 - 0.3 mm.) and non-ferroan. Typically it destroys the original texture, although occasionally this may be crudely preserved. The dolomite replacing the finer grained beds of the Clydach and Daren Ddu Beds is likewise fine grained as are the dolomite pods in the concretionary horizons. Some of the dolomitisation seen is associated with faulting, only occurring in the vicinity of the faults. The dolomite in such areas is very coarse (approx. 3 mm.) with good rhombic outlines visible both in hand specimen and in thin section.

Voids in the dolomites, both primary and secondary, may be filled or partly filled with sparry calcite. This is described in 4.2.

There are often signs of dedolomitisation, the dolomite being replaced by ferroan calcite that is brightly luminescing (Fig. 4/1a). Elsewhere, where the rock only contains scattered dolomite rhombs, these may have been completely removed to leave dolomouldic porosity. The lack of any filling in the dolomoulds suggests that this is a recent, near surface affect (Evamy, 1967; Groot, 1967).

It is thought that the majority of the dolomitisation occurred prior to the precipitation of Zone 6 cement. The following evidence supports this:

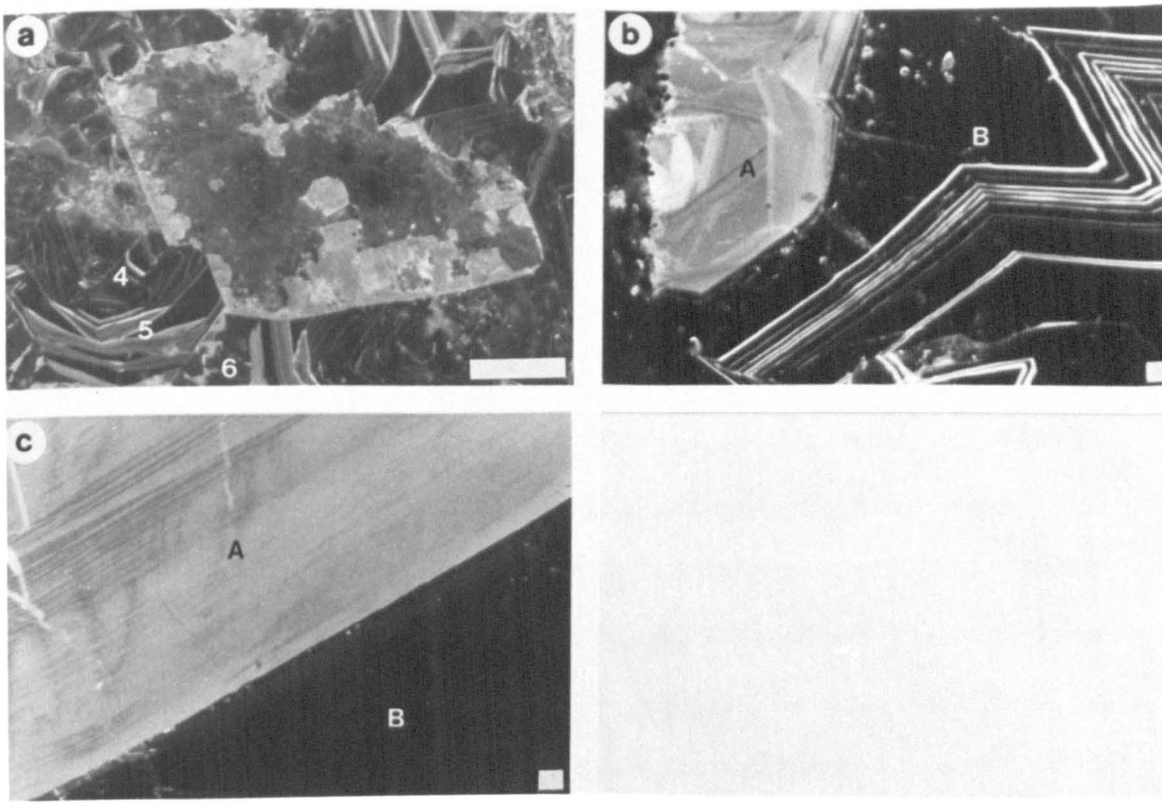
1. considerable porosity exists in some of the dolomites. Much of this porosity occurs as shelter cavities below former shells and is primary; it is not the result of volume reduction associated with the transformation of calcite to dolomite. In rocks that are thought to be undolomitised equivalents of these, shelter cavities are completely filled by Zone 6 cement. Therefore, it is presumed that dolomitisation occurred prior to the precipitation of Zone 6;
2. in rocks that are only partially dolomitised, the dolomite rhombs are restricted to replacing allochems; dominantly ooids. They cut across grain to grain contacts that resulted from pressure solution. Some such boundaries have Zone 2b cement trapped along them and the dolomite replaces this also. This suggests that dolomitisation occurred after the precipitation of Zone 2b cement.

Fig.4/1 DOLOMITE AND POST-DOLOMITE CALCITE

a)Dolomite rhomb cutting across Zone 4,5 and 6 calcites.The rhomb is being replaced by brightly luminescing calcite.Sample 18314.

b)The post-dolomite calcites have an initial brightly luminescing,ferroan zone (A),followed by a dominantly non-luminescing,non-ferroan zone (B).Changing crystal form is evident in A.Sample 17859.

c)The ferroan calcite of zone A shows a fine structure the origin of which is unknown.It is unlike 'normal' growth zonation in that the variously luminescing bands are irregular and discontinuous.The non-ferroan calcite of zone B is non-luminescing.Sample 20565.


a
4
5
6
b
A
B
c
A
B

Unfortunately the rocks that are dolomitised do not contain Zone 3, 4 and 5 cements and so it is impossible to date the dolomitisation relative to these.

The above interpretation agrees with that of George (1955) and Bhatt (1976) who both state that dolomitisation in the Clydach area occurred after burial. Neither suggest a depth at which they believe dolomitisation to have occurred although both suggest that it occurred during the Lower Carboniferous. Bhatt (1976) suggests a seepage-reflux model to account for dolomitisation, although this is strongly criticized by Wright (1981).

Dolomites that are associated with faulting cut across Zone 4, 5 and 6 cements where found within the Gilwern Oolite (Fig. 4/1a). These, therefore, occurred very late in the diagenetic history of the Oolite Group.

4.2 Post-dolomite calcite

Calcite is found filling and partly filling primary and secondary porosity within the dolomites and as a final filling to veins that are partly filled by dolomite that occur within the Pwll-y-cwm and Blaen Onneu Oolites and the Daren Odu Beds in the Clydach area. Stained thin sections reveal that there is a change in iron content with time. Initially the calcite is ferroan. Later calcite is non-ferroan. Occasionally this change is accompanied by the precipitation of pyrite. Calcite crystals are large; up to several centimetres long.

Two well formed specimens have been found. One was a scalenohedral crystal with an acute termination topped by a rhomb, in the fashion of sceptre quartz, with an obtuse termination (1011?), the other consisted of a prism with an obtuse termination (1011).

This suggests that changes in form have occurred during the growth of the crystals.

The CL of the calcite is as follows. The ferroan calcite is very brightly luminescing in several tones (Fig. 4/1b). It has a very fine microstructure (Fig. 4/1c), the origin of which is not understood. The non-ferroan calcite is non-luminescing but contains brightly luminescing hairline zones (Fig. 4/1b). The zonation pattern of the brightly luminescing calcite shows that it is scalenohedral. No good cross-sections of the non-ferroan calcite have been found, but this would appear to be rhombohedral. Within the dolomites the zones described above can be traced laterally. Calcites from the Daren Ddu Beds at Coed Pant-y-daren (Sample 20565) are virtually identical to that found in the Blaen Onneu Oolite at Daren Ddu (Sample 17859).

The calcites described above cannot be matched with any of the cements described previously although the luminescence of the non-ferroan calcite is very similar to that described for Zone 4 cements. It would seem that the pore fluids that precipitated calcite within the dolomites were confined to the dolomites. The presence of similar calcite within dolomites associated with faults as well as earlier dolomite suggests that the calcite postdates all the cements that were identified in 2.3. This would explain why this type of calcite is restricted to the dolomites; it was precipitated when the pore space in the majority of the Oolite Group had been filled. It is not clear why the pore space within the dolomite was not filled prior to the precipitation of post-dolomite calcites by the cement identified in the rest of the Oolite Group. Further information regarding the origin of this calcite is given in Chapter 7.

CHAPTER FIVE

CONCRETIONS

5.1 Calcrete

Occurrence

What is interpreted as a calcrete horizon is developed on top of the karst at the top of the Gilwern Oolite (Wright, 1980, 1981). It varies from 0 to 1.5 m in thickness. Calcrete-like material also occurs as a coating to blocks in the brecciated zone at the top of the Gilwern Oolite and as a pore filling (see 2.1).

Description

The calcrete is buff in colour and nodular, containing much green clay between the nodules. The nodules themselves only contain 3-5% acid insoluble residue, some of which is detrital quartz and authigenic pyrite.

The calcrete is composed of two distinct portions that can be identified by their respective grain sizes. The coarser averages 15 μm and the finer 5 μm (Fig. 5/1a, b). The coarser material occurs between fractured clasts of the finer material. Spar filled veins also cut the calcrete. These are dominantly filled by Zone 6 ferroan calcite, but occasionally Zones 4 and 5 calcite is present (Fig. 2/11a). The calcrete itself is dominantly non-ferroan, although in some areas it is ferroan. This is thought to result from solution/reprecipitation processes similar to those responsible for the formation of 'ferroan' ooids.

Fig.5/1 CALCRETE AND MASSIVE CONCRETIONS

a)Calcrete from the top of the Oolite Group.It consists of two components,one coarser than the other.Sample 18310.

b)Transmitted light photomicrograph of the area shown in (a).Sample 18310.

c)Brightly luminescing band crossing a massive concretion.It changes in form along its length.On the left it consists of a 'frilled' band,while on the right the brightly luminescing calcite is concentrated at the outer margin of rhombs.Sample 22365.

d)Transmitted light photomicrograph of the area shown in (c).There is a change in crystal fabric associated with the change in the CL nature of the brightly luminescing band.Sample 22365.

e)Close-up view of the left hand portion of the brightly luminescing band illustrated in (c).Sample 22365.

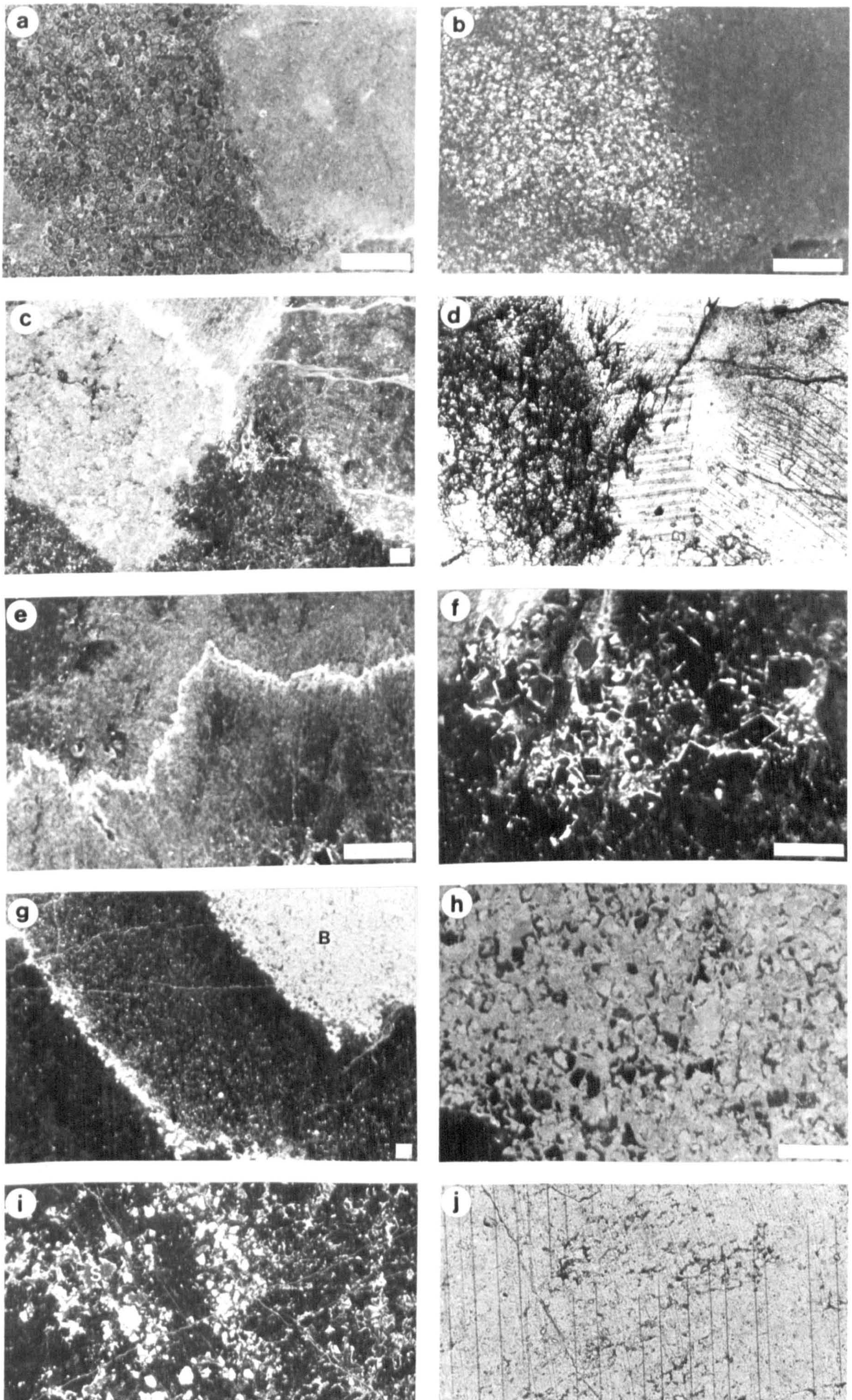
f)Close-up view of the right hand portion of the brightly luminescing band illustrated in (c).Sample 22365.

g)View across the margin of the black 'nucleus'(B) of a massive concretion.The black 'nucleus' has a very brightly luminescing.A brightly luminescing band is seen paralleling the margin of the 'nucleus'.Sample 17895.

h)Close-up of the black 'nucleus' illustrated in (g).Within it numerous rhombohedral outlines are visible.Sample 17895.

i)Part of a massive concretion.Solution vugs(S) are lined by brightly luminescing calcite and filled by dull luminescing calcite.Brightly luminescing calcite occurs in rhomb-shaped areas.Sample 22365.

j)Transmitted light photomicrograph of the area shown in (i).The area consists almost entirely of a single calcite crystal.Sample 22365.


a
b
c
d
e
f
g
B
h
i
j

Where the calcrete coats blocks or occurs as a pore filling it rests with a sharp contact against the oolite. Isolated ooids or oolite clasts, which sometimes occur within the calcrete, show little sign of calcretization.

The calcrete is brightly luminescent. The finer grained material has a uniform CL (Fig. 5/1a). It is impossible to identify individual grains using CL. The CL of the coarser material reveals that it is composed of zoned rhombs (Fig. 5/1a), probably of the 1011 form. The rhombohedral nature of the grains is not evident in transmitted light since they have grown together to form an interlocking, anhedral mosaic.

Discussion

Folk (1971) and Chafetz & Butler (1980) note the occurrence of calcrete nodules composed of rhombs. Folk (1971) believes these grew displacively. It is presumed that the calcrete developed in a soil horizon overlying the karst at the top of the Gilwern Oolite. There is no evidence that the oolite itself is replaced. Whether growth was displacive or replacive is unclear. The preservation of zonation in the rhombs is believed to indicate that they are primary, the variations in CL reflecting chemical variations in the groundwaters from which they were precipitated.

5.2 Daren Odu Bed concretions

Occurrence

Northwest of Darren concretions occur at two levels within the Daren Odu Beds. Both concretionary beds, one at the top and the other at the base of the Daren Odu Beds, are approx. 1 m. thick. At Darren, Chaw Pant-y-rhiw and Daren Cilau the concretions alternate with dolomite (Plate 1/1a, b), but further to the west than this the dolomite disappears.

<u>Description</u>

Three types of concretions are found in the Daren Odu Beds. These are composed of massive calcite, columnar calcite and botryoidal calcite. They are described in turn below.

Massive calcite concretions

These concretions are multi-coloured, containing reds, yellows, greens and browns in an overall marbled effect (Plate 5/1a, b). Such concretions are made up of several elements, listed below. A single concretion can contain any number and combination of these elements.

1. a sub-spherical, black 'nucleus',
2. multi-coloured non-ferroan calcite,
3. ferroan calcite filled vugs that have the same texture as elements 1 and 2. Inclusion-free ferroan calcite and/or pyrite pseudomorphs of a rhombic mineral (see 6.5) are often present,
4. columnar calcite, described later in the text, is often found in association with massive concretions,
5. cross-cutting veins.

Shale occurs between the concretions and is wrapped around them. Vertebrate debris can often be seen in cut and polished slabs. This can be separated by acid digestion. Insoluble residues so formed make up 5-7% of the concretions and also contain conodonts.

The bulk of the concretions are made up of crystals with a great range in size and shape. Crystals up to 5 mm. across are common. Shapes vary from equidimensional to markedly elongate. All crystals have sutured contacts and commonly contain carbonate inclusions that are not in optical continuity with the bulk of the crystal. Dark inclusions are common and suggest a former radial fibrous habit.

a

b

Plate 5/1 MASSIVE CONCRETIONS

Cut and polished surfaces of massive concretions from the Daren Ddu Beds at Craig y Cilau.The various elements that make up these concretions can be seen.Note especially the black 'nucleii' and the ferroan calcite filled vug (the green area to the left of the black 'nucleus') in (a).

Samples 17895 & 18348.

The crystals in the ferroan calcite filled vugs are also large, with sutured contacts. The only inclusion-free calcite occurs in pseudomorphs of former rhombic minerals, as a lining to ferroan calcite filled vugs and in veins that cut the concretions.

The concretions are dominantly non-luminescent, although concentric, brightly luminescing bands do occur (Fig. 5/1c, g). In one case the nature of this band changed abruptly along its length. This change is associated with a change in the fabric of the calcite crystals (Fig. 5/1c, d). Where the calcite contains inclusions defining a former fibrous structure the band has a sharp, 'frilled' appearance (Fig. 5/1e), but where the fibrous fabric disappears the band becomes diffuse and the bright luminescent calcite picks out many tiny, randomly oriented rhombs (Fig. 5/1f). Where these bands are seen in other concretions they have either one or the other of these textures. Due to the general lack of luminescence in most of the concretions it is impossible to make out the fabrics, but some areas seem to be completely made up of rhombs, although there is no indication of these in transmitted light. Occasionally scattered rhombic shaped areas contain brightly luminescent calcite (Fig. 5/1i, j). The black 'nuclei' have a very different CL to the bulk of the concretion. They are very brightly luminescent but again the luminescence gives the impression that the area is made up of many tiny rhombs (Fig. 5/1g, h).

The sparry calcite that grows around the ferroan calcite filled vugs shows normal growth zonation. The CL is consistent with Zones 4 and 5 calcite cements. A solution surface separates these two which correlates with Solution Event 4. Zone 4 calcite can be seen growing on top of the fibrous calcite. Much of the brightly luminescing calcite within the concretions is similar to Zone 5 calcite. Calcite within veins that cut the concretions can be correlated with Zones 4 onwards.

Columnar calcite

Columnar calcite occurs as sheets and in association with massive concretions (Plate 5/2a, b). The sheets have no preferred direction of growth; sheets develop both from the top and the bottom of the concretionary beds. Where columnar calcite crystals grow on massive concretions they often have a spherulitic habit. The crystals occur in a variety of colours similar to those seen in the massive concretions and include a white variety. Columnar calcite crystals have been found up to 22 cm long and 1 cm wide, but they are usually less than 10 cm in length.

The crystals taper slightly towards their base and have straight boundaries. Green clay and detrital quartz are often found between the crystals, especially in their outer portion (Plate 5/3a). Within this green clay a green mineral is found pseudomorphing a former rhombic mineral. It is pleochroic. The long axes of the rhombs and the fabric of the surrounding clay are usually aligned parallel to the sides of the crystals suggesting displacive growth. It has not been possible to separate sufficient of the mineral to identify it. Possibilities are chlorite and glauconite. Where the columnar calcite crystals protrude into the surrounding shale they have rhombohedral terminations (Plate 5/2b). Individual crystals have uniform extinction. Splays of crystals exhibit progressive extinction on rotation under crossed-polars.

The crystals have a clear, inclusion-free core, the cross-section of which is triangular like the crystals themselves (Plate 5/3a). The rest of the crystals are composed of inclusion-rich calcite that displays pseudopleochroism. The inclusions have a feather-like

a

b

Plate 5/2 COLUMNAR CALCITE CONCRETIONS

Cut and polished surfaces and the exterior surface of columnar calcite concretions.

a) The columnar crystals have been cut approx. parallel to their length. They are growing off of massive calcite concretions. Samples 18144 & 17890.

b) The columnar crystals have been cut approx. perpendicular to their length. Rhombohedral crystal terminations can be seen protruding on the exterior of the concretion. Sample 17896.

a

b

Plate 5/3 COLUMNAR CALCITE

Transmitted light photomicrographs of stained thin sections.

a) Columnar calcite crystals cut perpendicular to their length. There is a clear, inclusion-free core in the centre of each crystal that has a triangular cross-section. The outer portion of the crystals consist of inclusion-rich calcite. Green clay is trapped between the crystals. Sample 18145. Scale bar represents 5mm.

b) Columnar calcite crystals cut parallel to their length. A clear, inclusion-free core runs through the centre of each crystal. Inclusion-free bands run across the crystals perhaps reflecting former crystal faces. Irregular areas of ferroan calcite (blue) are thought to be filled solution vugs. Sample 17895. Scale bar represents 5mm.

distribution, being inclined towards the inclusion-free core and away from the direction of growth (Plate 5/3b). The inclusions are thought to outline former fibres. Detrital quartz grains are scattered throughout the crystals and behind these there is, on occasions, a 'shadow zone' in which the calcite is free of inclusions (Fig. 5/2b). The 'shadow zone' is elongated in a direction parallel to the trend of the inclusions. At irregular intervals inclusion-free bands traverse the splays of columnar calcite crystals. These seem to be defining former crystal faces (Plate 5/3b).

Inclusion-free and inclusion-rich calcites are cut indiscriminantly by numerous straight twin lamellae (Plate 5/3b, Fig. 5/2b).

Staining shows that the crystals are dominantly non-ferroan. Ferroan calcite is found occupying irregular areas that are thought to be Type 1 solution vugs (Plate 5/3b). The edges of the crystals also tend to be slightly ferroan. Areas of ferroan calcite parallel the trend of the inclusions. The shape of these areas, that are the result of solution, is controlled by the former fabric of the crystals and hence represent Type 2b solution features. Ferroan calcite is thought to be of Zone 6 age.

The columnar calcite is mainly non-luminescent, but irregularly spaced, very brightly luminescent bands run across the crystals (Fig. 5/2a, c, e). The shape of these possibly define former crystal faces. The intensity of the luminescence in these bands gradually builds up then there is an abrupt return to non-luminescent calcite. The luminescent bands on some occasions show fine structure. The bands cut across the fabric of the crystals and generally appear to be unrelated to the inclusion-free bands that run across the crystals. The margins of the crystals contain dull to brightly luminescing

Fig.5/2 COLUMNAR CALCITE

a) Very brightly luminescing band crossing columnar calcite crystals. Detrital quartz grains(Q) are trapped within the crystals. The upper margin of the bright band is irregular suggesting etching. Sample 20580.

b) Transmitted light photomicrograph of the area shown in (a). The calcite is inclusion-rich except in 'shadow-zones' behind detrital quartz grains(Q). The inclusions pick out a former fibrous structure. The direction of growth is upwards. Sample 20580.

c) Very brightly luminescing band crossing columnar calcite crystals in a massive/columnar concretion. Possible former crystal faces are outlined. There is a gradual build-up in luminescent intensity then a sharp return to non-luminescing calcite. Locally, the outer margin of the band is irregular suggesting etching. Sample 18348.

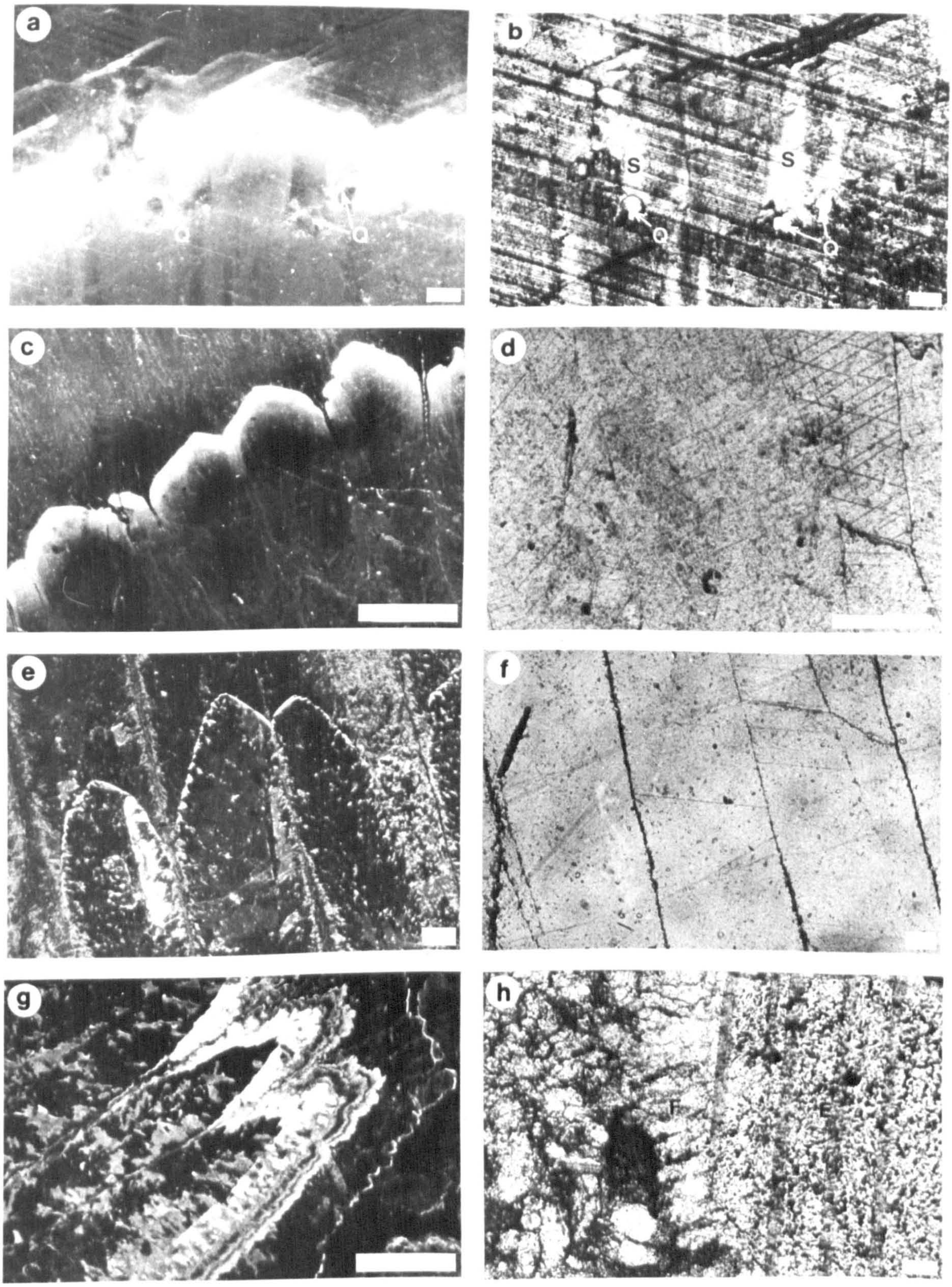
d) Transmitted light photomicrograph of the area shown in (c). There is no evidence of the band visible with CL. Sample 18348.

e) Columnar calcite crystals. A brightly luminescing line picks out possible former crystal faces. There is evidence of solution both above and below the line. Sample 22367.

f) Transmitted light photomicrograph of the area shown in (e). Sample 22367.

g) Columnar calcite occurring within a massive concretion. Areas of dull luminescing calcite cut across the zoning of the crystals and are aligned parallel to relic fibres in the crystals(not visible using CL). Sample 22367.

h) Transmitted light photomicrograph showing fibrous calcite(F) growing on an echinoderm fragment(E). Sample 17879.


a
O
O
b
S
S
O
O
c
d
e
f
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h
F
E

calcite in elongate areas that run parallel to the trend of the inclusions (Fig. 5/2e, g). These are the result of solution processes (see distribution of ferroan calcite above).

Botryoidal concretions

This type of concretion has a very limited distribution. It is only found in the lower concretionary horizon at the north end of Craig y Cilau and at Craig y Castell.

These concretions consist of a cluster of lobtate, green to brown calcite masses. Many may occur in a cluster (Plate 5/4a). The convex surfaces of the masses always face downwards. The horizontal dimensions of a single calcite unit fall between 1 and 4 cm; the vertical dimensions are commonly slightly less. Clay and detrital quartz separate each calcite unit. Occasionally the junctions are stylolitised. Partings in the clay are parallel to the sides of the calcite units.

Each calcite unit consists of an array of radiating, acicular crystals separated by dark material, probably clay, and contains scattered detrital quartz. The masses as a whole display sweeping extinction and twin planes curved in the direction of growth. The centre of each calcite unit contains white sparry calcite which spreads outwards in a series of radiating veins which become thinner outwards (Plate 5/4a, b). The sparry calcite crystals show abundant evidence of deformation (undulose extinction, deformed twin lamellae).

Staining shows that the radiating acicular crystals are dominantly non-ferroan although there may be an increasing amount of ferroan calcite towards the outer margin where it occurs as elongate areas extended in the direction of the fibres (Plate 5/3b). The sparry calcite is mainly non-ferroan but there is a ferroan zone

a

b

Plate 5/4 BOTRYOIDAL CONCRETIONS

a) Cut and polished surface and exterior surface of botryoidal concretions from the Daren Ddu Beds at Craig y Castell. The concretions consist of aggregates of hemispherical units. The centre of each unit is fractured and contains inclusion-free calcite (white). Sample 17908.

b) Transmitted light photomicrograph of a stained thin section. Each hemispherical unit consists of acicular, inclusion-rich calcite, here slightly ferroan (blue) at its outer margin, and inclusion-free calcite in the fractured centre of the units. This is largely non-ferroan (pink), although later calcite is ferroan. Saddle dolomite (turquoise) occasionally forms a final fill. Sample 17910. Scale bar represents 5mm.

at the inner edge of the calcite and the final fill is also often ferroan. Occasionally baroque dolomite occurs after the ferroan calcite (Plate 5/3b).

The acicular calcite is dominantly non-luminescent as the sparry calcite. The ferroan calcite has dull luminescence although where patchy it contains irregular areas of brightly luminescent calcite. The baroque dolomite is non-luminescent.

Discussion

The diagenetic history of the concretions is complex and not fully understood. They were formed prior to the precipitation of Zone 4 calcite since Zone 4, 5 and 6 calcite are found filling fractures within the concretions. The concretions must be formed at shallow depth although they may not be 'early' as defined in this study.

The presence of abundant conodonts in the shales and concretions indicates that they grew within marine deposits. However, this does not mean that the concretions themselves are of marine origin (Clark, 1981). The way in which the shale wraps around the concretions and the presence of dark material, probably clay, between what appear to have been calcite fibres suggests that they grew mainly displacively within the shale horizon. The colour of the concretions may result from variations in the included clay material. The colours are similar to those described by Wright (1981) for clays from subaerial exposure surfaces in the Llanelly Fm and are similar to those occurring at penecontemporaneous subaerial exposure surfaces within the Oolite Group.

The rhombic fabric that is evident with CL is similar to the fabric seen in the calcrete at the top of the Gilwern Oolite. If this fabric is primary it would suggest formation within a soil horizon. However, many randomly oriented, rhombic outlines occur within the crystals that exist today. Presuming that the rhombic fabric is primary, this would require recrystallisation of the concretion without redistribution of the elements responsible for the CL. A brightly luminescent band has been described that changes both its transmitted light and CL fabric along its length. It is thought that this change is caused by partial recrystallisation. In this case it seems more likely that the area showing relict fibres and a sharp luminescent band is not recrystallised, whereas the area with large, sutured crystals and a diffuse luminescent band made up of rhombs is recrystallised. There is, therefore, some doubt as to the origin of the rhombic fabric seen with CL.

The columnar calcite is similar to calcite layers and cone-in-cone calcite described by Woodland (1964), Franks (1969) and Marshall (1982). The distribution of inclusions in the columnar calcites and the occurrence of inclusion-free 'shadow zones' behind detrital quartz grains suggests their original fibrous nature. The products of the recrystallisation of fibrous carbonate have been described by Kendall & Tucker (1973), Kendall (1977), Kendall & Broughton (1977). The fibres probably occurred as laterally interfering bundles. The 'shadow zones' result from fibrous calcite coming up against detrital quartz grains. The force of crystallisation was insufficient to move them and further growth was halted. This would leave an area behind the quartz grain which contained no calcite. If this is the case and assuming that the premise that the fibrous crystals developed within a clay sediment is correct, one would expect that the 'shadow zones' and other areas where fibres have not displaced the clay should be filled with clay rather than inclusion-free calcite. Inclusion-free calcite would only be expected filling secondary voids. Therefore, the exact origin of the 'shadow zones' is unclear. Possibly they are secondary, rather than primary, in origin.

Inclusion-free bands run across the crystals and these may be primary or secondary in origin. In the former case the clear zones would develop by the true displacive growth of large crystal faces within the sediment. Inclusion-rich areas would result from the displacive growth of fibrous crystals. It is known that in speleothem calcite fibrous calcite growth and coalesence may be virtually simultaneous (Folk & Assereto, 1976; Kendal & Broughton, 1977, 1978). It is possible that recrystallisation of fibrous calcite, in the Daren Ddu Bed concretions, occurred shortly after its formation. The development of crystal faces on, and the continued growth of the secondary crystals would result in the clear zones that are seen today. Alternatively Kendal & Tucker (1973) describe variations in inclusion density that are the result of recrystallisation that may have occurred long after the growth of the original fibrous calcite. Either explanation is possible. The presence of bands with bright CL that also run across the crystals, although not in the same places as the inclusion-free zones, is probably also the result of recrystallisation, the bright bands being analogous to the concentric bright bands seen in the massive concretions. The origin of the clear core of the crystals is unclear. The distribution of inclusion-rich and inclusion-free calcite is similar to that described by Kendall & Broughton (1978) for recrystallised speleothem. The angle of the relic fibres makes a direct comparison of these two occurrences difficult though. It must be concluded that many aspects of the development of the concretions and columnar calcites remain unclear.

Botryoidal concretions result from the largely displacive growth of radiating, fibrous bundles. The reason for their restricted distribution and unidirectional growth direction is unknown. The fractures in the centres of the fibrous bundles are visually similar to those developed in septarian nodules. Sparry calcite filling these fractures is probably of Zone 4 age; this restricts the time at which they grew.

5.3 Blaen Onneu Oolite concretions

Occurrence

A nodular horizon approx. 1 m thick occurs at the top of the Blaen Onneu Oolite between Darren and Daren Cilau (Plate 1/1a). Further west than this the horizon is not seen. This is initially due to lack of exposure, but also because erosion prior to Llanelly Fm. deposition removed the top of the Oolite Group. Eastwards from Darren the nodular horizon is laterally replaced by dolomite lenses similar to those seen in the Daren Ddu Beds inthe Chaw Pant-y-rhiw area (Plate 1/2).

Description

The nodules in this horizon are tightly interlocking. They vary greatly in size, from 5 cm to more than 20 cm in diameter. Polished cross-sections of two nodules are shown in Plate 5/5a, b. The nodules are light green in colour. Acid digestion reveals the absence of marine biological insoluble residue. They often have a poor concentric structure formed by alternating fibrous and non-fibrous calcite. The fibrous calcite crystals tend to be restricted to the outer portion of the concretions. The fibres are triangular in cross-section with rhombohedral terminations where they occur at the outer edge of the nodule. Traces of burrows are occasionally

a

b

Plate 5/5 RECRYSTALLISED CALCRETE CONCRETIONS

Cut and polished surfaces of recrystallised calcrete concretions from the top of the Blaen Onneu Oolite at Chaw Pant-y-rhiw.

a) The orange areas are ferroan calcite filled vugs. The mottling in both concretions is due to the development of fibrous calcite. Samples 22366 & 17889.

b) This concretion is very similar to the massive concretions from the Daren Ddu Beds. Sample 17874.

seen within the nodules. These developed in the sediment prior to the development of the nodule. Small areas (approx. 1 cm diameter) contain lemon-coloured calcite. This is intensely ferroan and thought to be equivalent to Zone 6 cement. Similar ferroan calcite areas have been described from massive calcite concretions from the Daren Odu Beds.

Thin sections reveal that the bulk of the nodules are composed of calcite crystals with sutured contacts (as in the massive concretions from the Daren Odu Beds). There is a great variation in crystal size; up to 6 mm across. Crystals contain detrital quartz and carbonate inclusions. The fibrous calcite has straight crystal boundaries.

The nodules are dominantly non-luminescent; however, brightly luminescent concentric bands are present in some specimens (Fig. 5/3a). In these bands the brightly luminescent calcite is restricted to the spaces between rhombs which are themselves zoned with dull and non-luminescent calcite (Fig. 5/3b). A similar CL fabric has been described from the massive calcite concretions from the Daren Odu Beds. The patchy nature of the dominantly non-luminescent areas suggests that these too may consist of rhombs, but due to the lack of luminescent intensity they cannot be resolved. The bright bands coincide with the fibrous bands in the nodules (Fig. 5/3c,d). Casts of allochems can be distinguished in some areas. Once identified with CL they can also be distinguished in transmitted light (Fig. 5/3e, f). Sparry calcite crystals lining ferroan calcite filled vugs show CL similar to that seen in Zone 4. The zonation pattern is very irregular and suggests solution (Fig. 5/3g, h, i).

Fig.5/3 RECRYSTALLISED CALCRETE

a)Recrystallised calcrete concretion consisting largely of non-luminescing calcite.Diffuse,brightly luminescing concentric bands occur in the concretion.Sample 22366.

b)Close-up of brightly luminescing band.It consists of many,randomly oriented rhombs.The bright calcite occurs between the rhombs which are zoned with dull and non-luminescent calcite.Sample 22366.

c)Brightly luminescing band in recrystallised calcrete concretion.Sample 22366.

d)Transmitted light photomicrograph of the area shown in (c).The brightly luminescing band coincides with the fibrous calcite layer.Sample 22366.

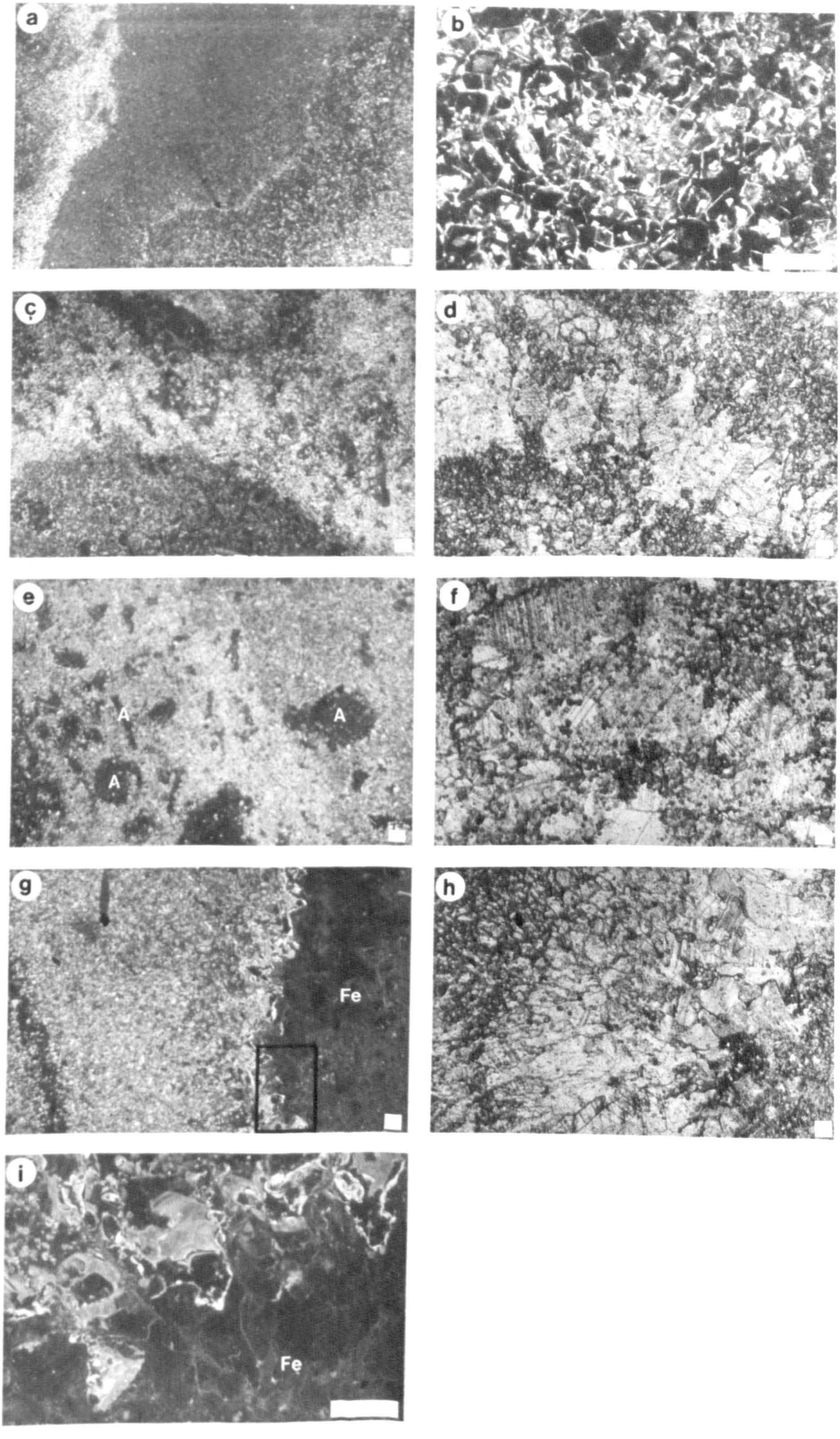
e)Relic allochems(A) are sometimes present.Sample 22366.

f)Transmitted light photomicrograph of the area shown in (e).The relic allochems evident with CL are hardly visible.Sample 22366.

g)The margin of a ferroan calcite(Fe) filled vug.Sparry calcite crystals appear to line the vug prior to ferroan calcite precipitation.Sample 22366.

h)Transmitted light photomicrograph of the area shown in (g).The margin of the ferroan calcite filled vug is no longer obvious.Sample 22366.

i)The area shown in the box in (g).The crystals lining the ferroan calcite(Fe) filled vug do not have a 'normal' zonation pattern.It is thought that the patchy CL pattern is the result of solution and the later filling of solution vugs.Sample 22366.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Discussion

These concretions are similar in many ways to the massive concretions of the Daren Odu Beds. The preservation of structures that were present in the original sediment, i.e. burrows, suggests that growth of the concretions was not displacive. However, such structures are exceedingly rare. The origin of the rhombic CL fabric has been discussed earlier in this chapter. It is not known why brightly luminescent bands are associated with concentric fibrous layers. These are presumed to be recrystallisation features. The development of radial fabrics by recrystallisation has been described by Chafetz & Butler (1980); however, unlike their example recrystallisations appears to be from the centre outwards rather than the outside inwards because fibrous calcite crystals taper towards the interior of the concretions. This is consistent with other examples from the Oolite Group.

It is thought that the nodules represent a recrystallised calcrete. It is not possible to say whether the rhombic fabric seen with CL is primary or secondary.

5.4 Conclusions

1. There are a number of horizons within the Oolite Group at which concretions occur. Those at the top of the Gilwern and Blaen Onneu Oolites are probably associated with subaerial exposure. Those in the Daren Odu Beds have a problematical origin.
2. All concretions are cut by veins containing Zone 4 calcite. They must have formed prior to or during the precipitation of Zone 4 calcite.
3. Recrystallisation has modified most of the concretions found in the Oolite Group; those at the top of the Gilwern Oolite being the exception.

4. Columnar calcite crystals are similar to cone-in-cone calcite and calcite beef suggesting they are purely diagenetic in origin.
5. CL of the concretions reveals fabrics that otherwise cannot be seen. However, this has not clarified the origin of many of the concretions; rather it has made them more difficult to interpret.
6. Carbon and oxygen isotopic analysis of samples from concretions is discussed in Chapter 7. This sheds little light on the origin of the concretions.

CHAPTER SIX

AUTHIGENIC MINERALS

An 'authigenic mineral' is taken to mean a non-carbonate mineral that has been precipitated in or has replaced the sediment during diagenesis.

6.1 Quartz

Occurrence

Authigenic quartz occurs in two forms:

1. euhedral crystals - these are variable in size; the long axes of the crystals are between 70 and 400 µm. and sections perpendicular to this are 20 and 90 µm. across. They occur as well developed prisms with pyramidal terminations (Fig. 6/1a, b). The crystals occur individually or in clusters (Fig. 6/1b). They occur almost exclusively within ooids and micritic clasts, although they may be found growing across cement between such allochems. There is no evidence of there being original detrital cores in these quartz crystals. The quartz is often cloudy due to the presence of numerous tiny inclusions. Where the quartz replaces calcite spar the inclusions are often much larger (Plate 6/1a). The tiny inclusions often ghost the margins and structure of the ooids they have replaced;

Fig.6/1 AUTHIGENIC QUARTZ AND FELDSPAR

a) SEM photomicrograph showing the termination of an authigenic quartz crystal. As well as the major pyramidal faces present there is also a subsiduary pyramidal face present. The dimpling of the surface of the crystal is thought to be due to the solution of carbonate inclusions on the surface of the crystal. Sample 20583.

b) SEM photomicrograph of a cluster of euhedral, authigenic quartz crystals. The termination shown in (a) is identified by the box. Good prism faces are developed. Sample 20583.

c) SEM photomicrograph of a cluster of authigenic feldspar crystals. Sample 17865.

d) SEM photomicrograph showing elongate authigenic feldspar crystals. These do not show well developed crystal form, unlike the equant authigenic feldspar crystals shown in (c). Sample 17865.

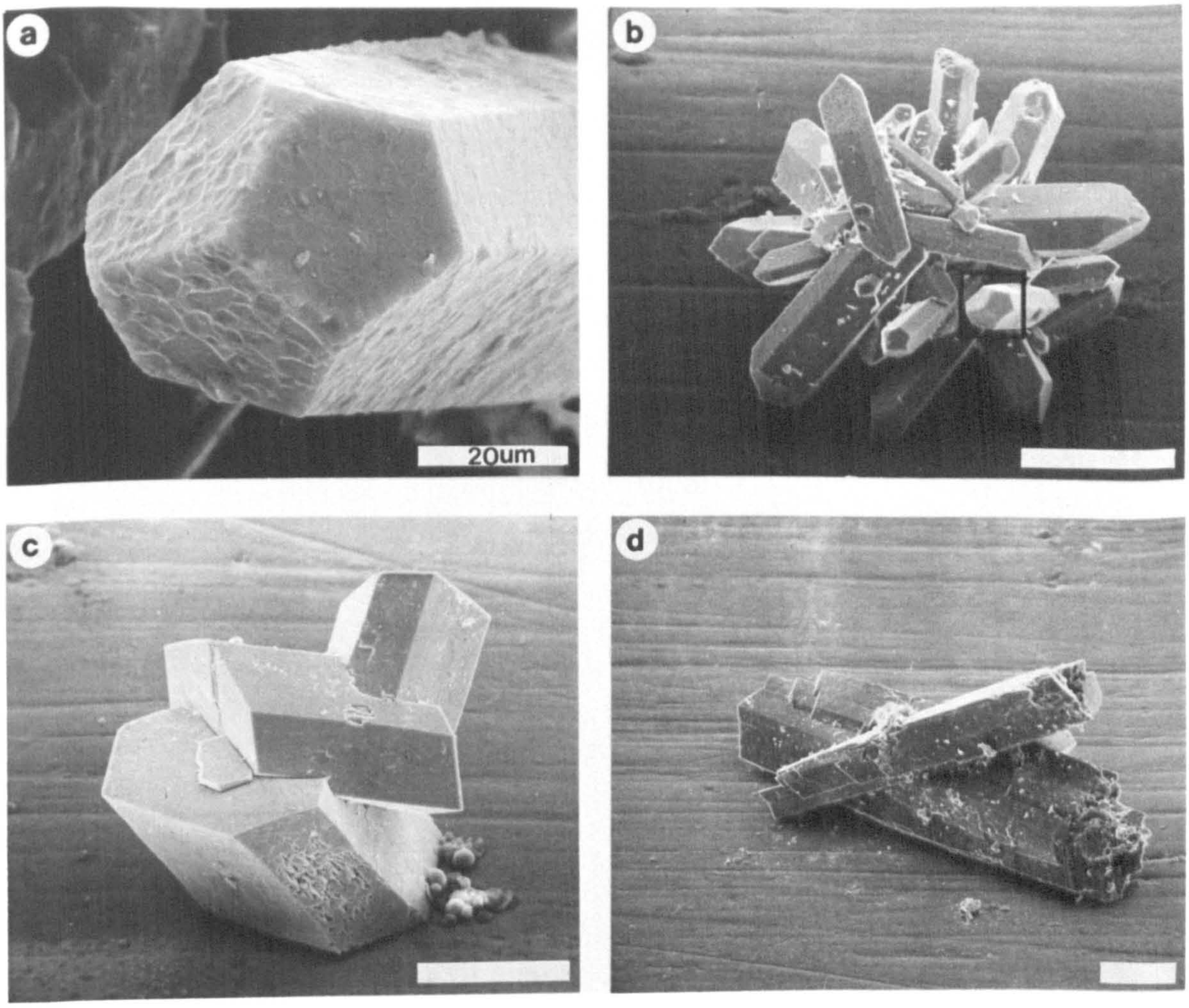

a
20um
b
c
d

Plate 6/1 AUTHIGENIC QUARTZ

Transmitted light photomicrograph of a stained thin section. A euhedral authigenic quartz crystal is replacing ooids and calcite spar. Where ferroan calcite is being replaced inclusions within the quartz are also ferroan (blue). Where non-ferroan calcite is being replaced inclusions within the quartz are also non-ferroan (pink). This indicates that the quartz formed after the precipitation of ferroan calcite (Zone 6). Sample 20539.

2. microcrystalline - this type of quartz is found replacing brachiopod valves. In the replacement process the structure of the valves is retained (Plate 6/1b). This type of quartz is seen throughout the Oolite Group but is not necessarily associated with euhedral quartz. There is a close correlation between the development of microcrystalline quartz and the presence of solution holes filled with Zone 6 calcite within the replaced brachiopod valves.

Discussion

Plate 6/1a illustrates an euhedral quartz crystal cutting across ooids and cement. Where it cuts across ferroan calcite spar it contains ferroan calcite inclusions and where it replaces non-ferroan calcite spar it contains non-ferroan calcite inclusions. This suggests that the quartz grew after the precipitation of the Zone 6 ferroan calcite. A late diagenetic origin is consistent with the widespread distribution seen within the Oolite Group.

The reason for the correlation between the occurrence of micro-crystalline quartz and solution holes within brachiopod valves is not known. It is unclear whether the microcrystalline quartz is of the same age as the euhedral quartz.

The replacement of limestone by silica is a common and well documented event (Graf & Lamar, 1950; Swett, 1965; Wilson, 1966). Depositional grains composed of material with small crystal size are preferentially replaced, e.g. ooids, micrite, although replacement post-dated porosity occlusion. This could reflect a variety of textural, compositional and chemical factors and hence the reason for this is unclear.

The source of silica is unknown. There is no evidence of it originating within the Oolite Group, e.g. as sponge spicules.

6.2 Feldspar

Occurrence

Only one sample collected contained authigenic feldspar, this was from the top of the Gilwern Oolite at Craig y Gaer (Sample 17865). Cross-sections through crystals have a variety of shapes, rhombs and hexagons being the most common (Fig. 6/2a,b). Occasionally the crystals are elongate (Fig. 6/1d). Rhombic sections have an average width of 0.1 - 0.2 mm, elongate crystals are up to 0.7 mm long. As with the authigenic silica, ooids and micrite are replaced preferentially by the feldspar. Where the feldspar crystals lie across ooid-cement boundaries, the junction is preserved as a line of inclusions. Occasionally inclusions ghost ooid structure. Examination under crossed polars reveals twinning (Fig. 6/2c, d) similar to that described by Kastner & Waldbaum (1968). No detailed optical work has been done on the twins. Detrital cores are not detectable either in transmitted light or using CL. The crystals are non-luminescing. The crystals typically have adularia-like habit and occur either singly or in clusters (Fig. 6/1c).

Microprobe analysis shows that 98% of the alkali in the feldspar is potassium.

Discussion

The occurrence of authigenic feldspar described above is very similar to that described by Kastner & Waldbaum (1968) and Kastner (1971). The feldspars found in the Oolite Group are typical in that they are a very pure end member; however potassium feldspars are relatively rare, compared to albite, as authigenic minerals in carbonate rocks. Also, the size of the crystals found

Fig.6/2 AUTHIGENIC MINERALS

a)Transmitted light photomicrograph showing the cross-section of an authigenic feldspar crystal that is replacing micrite.The crystal is twinned.Sample 17865.

b)Transmitted light photomicrograph showing the cross-sections of two authigenic feldspar crystals.The rhombic shape is typical.Sample 17865.

c)Transmitted light photomicrograph of the same area as shown in (b) but viewed under crossed polars.Note the unusual twinning.Sample 17865.

d)Transmitted light photomicrograph of the same area as shown in (b) but rotated by 30^{o} and viewed under crossed polars.Sample 17865.

e)Transmitted light photomicrograph showing framboids resting geopetally at the base of oomoulds filled with ferroan calcite (Fe).Sample 18344.

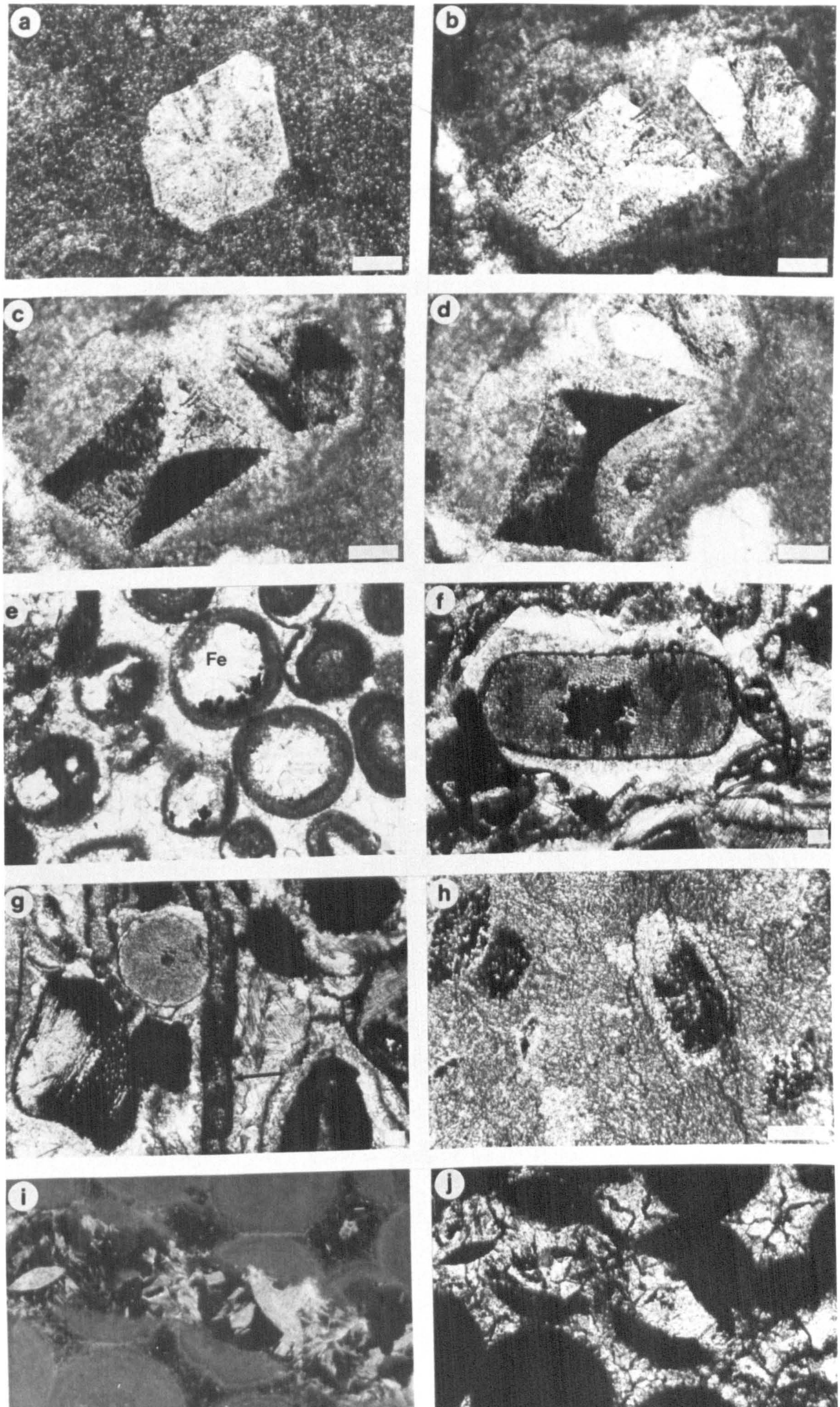
f)Transmitted light photomicrograph showing pyrite filling and replacing the centre of an echinoderm fragment.Sample 17830.

g)Transmitted light photomicrograph showing pyrite filling and replacing an echinoderm fragment.Pyrite is also present within the bivalve(?) mould (arrow).Sample 17830.

h)Transmitted light photomicrograph showing pyrite pseudomorphing gypsum within ferroan calcite from a vug in a concretion from the Daren Ddu Beds.Sample 17895.

i)Pseudomorphs of lenticular gypsum crystals occur within a vein filled with Zone 6 calcite.The pseudomorphs are brightly luminescing.Sample 18316.

j)Transmitted light photomicrograph of the area shown in (i).The lenticular pseudomorphs contain abundant dark inclusions.Sample 18316.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j

is much larger than the mean of 20 - 100 µm. quoted by Kastner (1971).

The geochemistry of authigenic feldspar precipitation is discussed by Kastner (1971). Although it is possible to produce authigenic feldspar at room temperature, it is more likely that they formed during burial. There is no petrographic evidence to suggest when they formed. However, it seems likely that they may be coeval with the authigenic silica since, during this time, there was obviously a sufficient supply of silica in solution. The very restricted distribution of the feldspar is a problem. It most likely reflects a restricted supply of potassium and aluminium. High values of potassium and aluminium cannot have been a general feature of the pore waters at the time of authigenic feldspar formation since this would have resulted in a wider occurrence of this mineral. A possible source of potassium and aluminium is from clays (Carrozi, 1960).

6.3 Glauconite

Occurrence

Glauconite has a very restricted occurrence. It is found in two forms:

1. filling and replacing echinoderm plates - it only occurs like this in the basal levels of the Daren Odu Beds in the Darren - Chaw Pant-y-rhiw area. It is most abundant in the centres of echinoderm plates (Plate 6/2), often being absent from the periphery of the plate;
2. pseudomorphing rhombs - this form is only found within clays trapped within the concretions of the Daren Odu Beds and is discussed in 6.5.

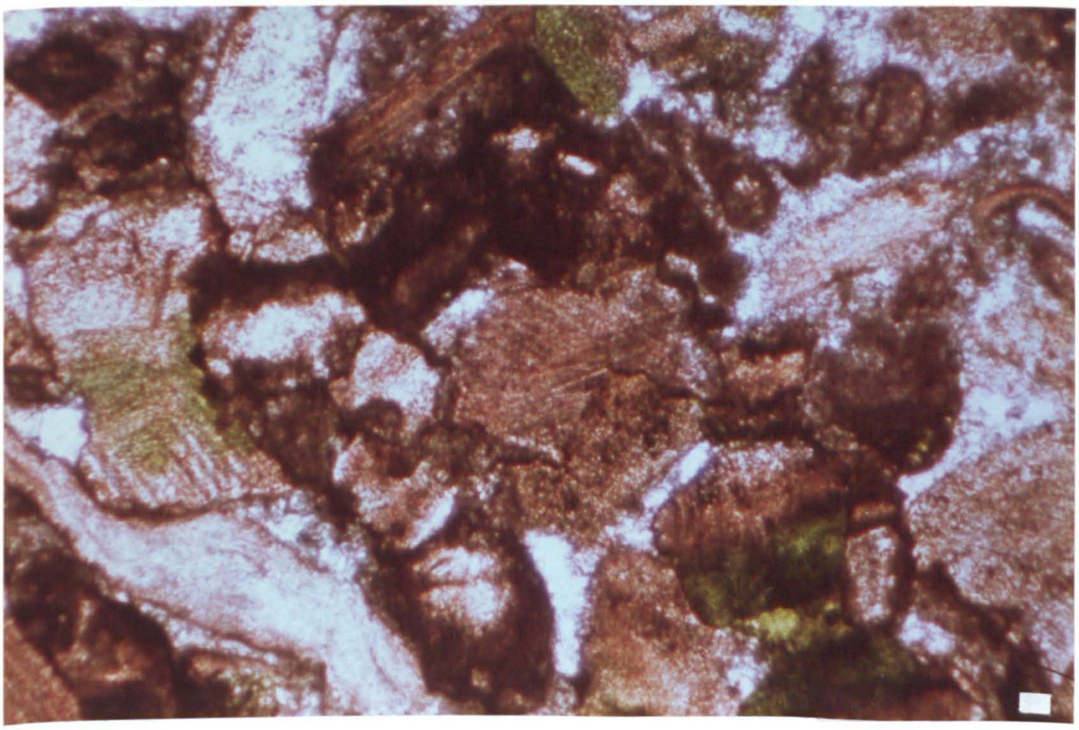


Plate 6/2 AUTHIGENIC GLAUCONITE

Transmitted light photomicrograph of a stained thin section. Echinoderm fragments are infilled and replaced by glauconite(green). Sample 17879.

Discussion

The presence of glauconite filling the stereome system suggests that it grew prior to any cementation and thus is 'early' diagenetic. Berry (1940), Pratt (1962), Seed (1965), Lamboy (1975) and Odin & Matter (1981) all record glauconite filling and in some cases replacing echinoderm tests. The latter authors also note the tendancy for glauconite to occur preferentially in the centre of grains and considered that glauconite needed an environment that was 'confined' from normal marine water in which to form. In other words a micro-environment existed at the centre of the echinoderm grains that favoured glauconite formation. Since glauconite invariably forms during early diagenesis this micro-environment may well have resulted from the decay of organic matter within the stereome. Such an environment would be reducing, although the environment outside the grain may be oxidising. A reducing environment has been favoured by many authors for glauconite formation (reviewed by Cloud, 1955). Also a pH of 7-8 would seem to be desirable and a source of iron is required, there being little or none in the substrate.

Glauconite is not a reliable depth or temperature indicator occurring, as it does today, from 65^{o}S to 80^{o}N and, most commonly, at depths between 50 and 500 m. However, it does indicate relatively shallow water with low sedimentation rates and a lack of turbulence. It is thought that the most favourable temperatures of formation are between 15 and 20^{o}C (Cloud, 1955; Porrenga, 1967; Odin & Matter, 1981). Very shallow tropical seas are too warm to encourage its formation.

The mode of origin of glauconite has recently been reviewed by Odin & Matter (1981). They view the 'layer lattice' theory of Burst (1958a,b) as generally incorrect, being only a special case, and consider that glauconite grows within pores and later replaces substrate as a result of solution. This is consistent with the occurrence of glauconite within the Daren Odu Beds where there is no evidence of sheet silicates either filling stereome systems or between grains as would be required by the 'layer lattice' theory.

The occurrence of glauconite at this horizon suggests that the environment of deposition was one of low sedimentation rates and quiet waters, perhaps a restricted lagoon or embayment. Modern examples suggest that the water depth was at least 30 m, especially bearing in mind the equatorial position of S. Wales during the Lower Carboniferous which would have meant that shallower water would have been too warm for glauconite formation. The exact nature of the environment in which the glauconite bearing sediments of the Daren Odu Beds were deposited is not known. They are in close association with sediments that are thought to be of possible intertidal origin. This suggests that they were deposited at considerably less than 30 m.

6.4 Pyrite

Occurrence

Authigenic pyrite occurs in four forms:

1. framboids - subspherical aggregates of crystals. Pyrite of this type is found within sparry cement. In some instances it rests geopetally on the floors of oomoulds (Fig. 6/2e). This suggests formation prior to Zone 6 calcite was precipitated since this is the encompassing cement;

2. euhedral crystals - these occur individually and in clusters. The crystals are typically octahedral although cubes are also found. They occur in the same way as framboids;
3. infilling and replacing allochems - irregular patches fill and replace biogenic allochems, notably echinoderm plates (Fig. 6/2f,g), bryozoa and ostracods. Examples that have been dissolved out are spikey and have irregular, branching form. These are thought to be casts of the stereome system of echinoderm plates. Pyrite of this type is very restricted in occurrence, being confined to the Blaen Onneu and Pwll-y-cwm Oolites in the Clydach area, where they contain suitable substrates, and rare occurrences in the Daren Ddu Beds. This type of pyrite must have been synsedimentary. otherwise the pores would have been filled with cement;
4. pseudomorphing a rhombic mineral - clusters of pyrite are seen pseudomorphing rhombic and lenticular crystals. These are common within concretions from the Daren Ddu Beds (Fig. 6/2h), but are also found elsewhere. The age of the pyrite is similar to that of Type 1 and 2 pyrite. These pseudomorphs are considered further in 6.5.

Discussion

Pyrite is a common authigenic mineral in sediments and sedimentary rocks. It commonly forms in reducing environments during early diagenesis by the bacterial reduction of seawater sulphate and reactions with Fe^{2+} (Berner, 1970). Although organic matter is commonly associated with pyrite formation it is not essential. It only acts as a source of energy for sulphate reducing bacteria. Framboids have been formed experimentally without biotic intervention (Berner, 1969; Sweeny & Kaplan, 1973).

The most likely source of sulphate is from seawater, organic sulphur is insignificant. The precipitation of substantial amounts of pyrite, especially in early diagenesis, would require a low sedimentation rate to maintain the supply from seawater by diffusion. Although seawater is by far the most important source of sulphate, locally other sources may be important. The association of pyrite pseudomorphing a rhombic mineral suggests that the original mineral may have been a sulphate source, i.e. gypsum.

The formation of pyrite within biogenic debris may be related to the decomposition of organic matter associated with allochems, as suggested for glauconite. This would produce a suitable micro-environment for sulphate reduction and pyrite formation. The environment outside the allochems need not have been reducing. There is a strong positive correlation between the distribution of Type 3 pyrite and the distribution of Zone 1 and 2b cements (Fig. 2/22). Zone 1 is in fact strongly ferroan indicating a reducing environment during its precipitation. However, it was not precipitated until after the deposition of the Blaen Onneu Oolite and the pyrite may well pre-date this.

The most common occurrence of pyrite in the Oolite Group occurs between Solution Event 4 and the precipitation of Zone 6 cement. Types 1, 2 and 4 pyrites are developed at this time. Single and clustered crystals and framboids have been described by Love and Amstutz (1966) and Sweeny & Kaplan (1973), however these are developed during early diagenesis. This pyrite grew during 'late' diagenesis and postdates much of the cement in the Oolite Group. It is probable that most, if not all, of the original organic matter within the sediment had been oxidised by this time. The reduction of sulphate required to form this pyrite may have been accomplished by the introduction of fresh organic matter brought in with the diagenetic sediment that was introduced at a similar time.

6.5 Gypsum pseudomorphs

Occurrence

Pseudomorphs of former rhombic and lenticular minerals occur in several forms:

1. replaced by granular pyrite in association with ferroan calcite (see 6.4) (Fig. 6/2h). This form is commonly found within ferroan calcite vugs in concretions, although they are occasionally found elsewhere;
2. replaced by sparry ferroan calcite - within the inclusion-rich ferroan calcite filling vugs in the concretions of the Daren Odu Beds there are occasionally rhombic to lenticular shaped areas that are inclusion-free. The boundaries between ferroan calcite crystals on occasions cut across such rhombic areas. This type of pseudomorph often occurs in association with that described in(1) above;
3. replaced by calcite containing many dark, unidentified inclusions - lenticular areas containing dark material are found in a ferroan (Zone 6) calcite vein from near the top of the Gilwern Oolite at Twyn-y-dinas (Fig. 6/2i,j). The inclusion-rich areas are very brightly luminescing;
4. replaced by glauconite (?) - see 6.3.

Discussion

The shape of the pseudomorphs, especially the lenticular ones, suggests that the original mineral was gypsum (Deer, Howie and

Zussman, 1966). Lenticular gypsum is common both in recent and ancient evapourite deposits. Type 1, 2 and 3 pseudomorphs indicate that gypsum was precipitated between the precipitation of Zones 5 and 6. It occurs within the diagenetic sediment introduced at this time. Although it formed during 'late' diagenesis this could not have been at any great depth. At depths greater than approx. 800 m. gypsum is unstable and anhydrite is formed instead (Berner, 1971). It is unlikely that the gypsum formed at anywhere near this depth since it is unlikely that the diagenetic sediment with which it is associated could have been washed down so far. The replacement of gypsum by pyrite indicates that it formed prior to pyrite formation.

The Type 3 pseudomorphs are brightly luminescing. Similar brightly luminescing calcite, associated with numerous dark inclusions, is common within Zone 6 cement (see 2.3). It may be that the two are connected and at least some of the brightly luminescing calcite is associated with the replacement of gypsum, the crystal shape having been lost. Alternatively, it may result from the replacement of fibrous gypsum; the occurrence of 'sheafs' of brightly luminescing calcite is mentioned in 2.3 (Fig. 2/15h). The deposition of gypsum requires the passage of hypersaline brines through the rock. The origin of these are unknown.

The lenticular form of gypsum is thought to result from its precipitation from alkaline solutions containing certain types of dissolved organic matter, e.g. humic acids (Cody, 1979). It was pointed out in 6.4 that the original organic matter within the sediment was likely to have been oxidised prior to the introduction of the diagenetic sediment in which the gypsum pseudomorphs are found. The organic matter required for the formation of lenticular crystals of gypsum must have been introduced with the pore waters from outside the study area. This has direct bearing on the formation of pyrite which occurred after gypsum formation. It illustrates that new sources of organic matter could have been introduced to facilitate the bacterial reduction of sulphate.

Unlike the other forms of gypsum the rhombs replaced by glauconite (Type 4) are likely to be relatively early in origin. Glauconite forms exclusively near the sediment-water interface. This type of occurrence of glauconite is very unusual and the author has found no reference to similar occurrences. It has been suggested previously that the concretionary horizons of the Daren Ddu Beds, in which this type of pseudomorph occurs, were deposited in the peritidal zone. The presence of gypsum in these rocks would be consistent with this idea, resulting from the evaporative concentration of marine derived porewaters. The origin of its replacement by glauconite is not understood. Certainly there is abundant glauconite elsewhere at these horizons (see 6.3).

CHAPTER SEVEN

CARBON AND OXYGEN STABLE ISOTOPES

7.1 Sampling and analysis

Individual components and cement generations were separated by cutting and/or scraping them from thin sections mounted in Lakeside 70 and stained with Alizarine red-S and potassium ferricyanide as described by Dickson & Coleman (1980), or by scraping from cut and ground blocks. Dickson & Coleman (1980) showed that the presence of stain and mounting medium in the sample does not affect the analysis. Inevitably the components separated will be contaminated by the calcite surrounding them, but hopefully this contamination is small. The more difficult it becomes to separate a component, because of its size, the more contamination becomes a problem.

The method of isotope analysis for the carbonates and the data corrections employed are similar to those normally used (McCrea, 1950; Craig, 1957; Clayton & Mayeda, 1963; Deines, 1970). In most cases the analytical uncertainty is about 0.02^{o}/oo for carbon and 0.03^{o}/oo for oxygen. Sampling errors will be considerably larger.

All isotope values are quoted against the PBD standard.

7.2 Allochems

Sample descriptions

Ooids, brachiopods and crinoid ossicles were sampled. Any special sampling procedures, important textural and minerallogical considerations and data from recent analogues are considered below.

Ooids

Ooids consist of two parts:

a) nucleus - usually bioclastic debris

b) cortex - inorganically(?) precipitated carbonate surrounding the nucleus.

Only the ooids with little or no visible nucleus were sampled so as to minimise contaminations from biogenic material.

The structure of the cortex of the ooids from the Oolite Group varies from radial-concentric to structureless; probably the result of varying amounts of micritisation. Modern marine ooids are composed of aragonite with the crystals tangentially oriented. Sanberg (1975) suggested that ancient ooids showing a radial arrangement of crystals were originally either low or high-Mg calcite. The original composition is important as this will control the original isotopic composition, since different carbonate minerals have different fractionation factors, and the way in which stabilisation to low-Mg calcite is achieved depends on the original mineralogy. Different stabilisation processes may cause different changes in $^{18}O/^{16}O$ and $^{13}C/^{12}C$.

Ooids will have an original porosity that will be filled with cement. Modern aragonite ooids have initial porosities as high as 50% (Bathhurst, pers. comm.). Although it is unlikely that radial ooids would ever have an original porosity that high, nevertheless, they are still composed of a mixture of ooid and cement. This problem is highlighted by 'ferroan' ooids where secondary porosity within the ooid has been filled with Zone 5 ferroan calcite.

Milliman & Barretto (1975) found relict high-Mg calcite ooids on the Amazon shelf with $\delta^{18}O = +1.2^{o}/oo$, $\delta^{13}C = +3.6^{o}/oo$. Modern aragonite ooids have been reported from the Bahamas with $\delta^{18}O = +0.2^{o}/oo$, $\delta^{13}C = +4.9^{o}/oo$ and from the U.S. shelf with $\delta^{18}O = +1.9^{o}/oo$, $\delta^{13}C = +4.3^{o}/oo$ (Deuser & Degens, 1969). It would seem that ooids are precipitated virtually in equilibrium with sea water.

Brachiopods

Brachiopod samples are of two types:

a) those from a single valve

b) those from many valves of varying species

In both cases punctate species were avoided as these would contain a non-skeletal component. Thin sections showed varying amounts of ferroan calcite 'replacing' valves (this is probably a solution/reprecipitation feature similar to that forming 'ferroan' ooids). Only valves containing little or no ferroan calcite were sampled.

Brachiopods deposit low-Mg calcite shells (Lowenstam, 1961; Milliman, 1974; Bathurst, 1975) in isotopic equilibrium with sea water (Lowenstam, 1961). Brachiopods should show the minimum isotopic alteration of any of the allochems, since they do not have to undergo stabilisation.

Crinoids

Abundant crinoid remains are rare in the Oolite Group, hence the lack of analyses. Separation was simple due to the large size of the ossicles. However, crinoid ossicles contain a pore system that is filled with cements of varying ages. In modern crinoids this can account for more than 50% of the volume (Bathurst, 1975). Therefore samples are a mixture of biogenic and inorganic material.

Modern crinoids are made of high-Mg calcite (Milliman, 1974). It is believed that ancient crinoids had a similar composition (Neugebaur, 1978), but that they have lost magnesium during diagenesis. As with ooids, the affect of this on the carbon and oxygen stable isotope ratios is unknown.

Strong biogenic fractionation of carbon and to a lesser extent oxygen is shown by modern crinoids. A mean value is $\delta^{13}C = -6.04^{o}/oo$, $\delta^{18}O = -2.39^{o}/oo$ (Weber, 1968). Not only do crinoids fractionate isotopes but the degree of fractionation varies between different parts of the skeleton (Weber & Raup, 1966). Since only stem ossicles were sampled it is unlikely that there is any variation in the isotopic ratios between them.

Modern crinoids are not good analogues for their ancient counterparts since they live in considerably more restricted and extreme environments.

Results

The results of the analyses of allochems are presented in Fig. 7/1 and are displayed graphically in Fig. 7/2.

The allochems have a wide range of values, none of them typical of precipitation in isotopic equilibrium with modern seawater. Some do show possible marine carbon values ($\delta^{13}C$ small and positive), but all have an oxygen value much lighter than would be expected ($\delta^{18}O$ small and positive). Not only is there great variation between the allochems, but also between the various rock units (Fig. 7/1 and 2).

POSITION	SAMPLE NO.	ooids		ferroan ooids		brachiopod		brachiopods		crin. ossicles	
		$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$
GILWERN OOLITE	17844	-4·74	-6·31	-4·49	-7·49	—	—	—	—	—	—
	17846	—	—	—	—	-2·65	-7·01	—	—	—	—
	17856 (a)	-3·81	-6·61	—	—	-3·81	-6·75	—	—	—	—
	(b)	-3·68	-6·62	—	—	—	—	—	—	—	—
	18341	—	—	—	—	-4·41	-6·93	—	—	—	—
(Coral Bed)	17862	—	—	—	—	—	—	-2·93	-6·20	-3·20	-6·06
	18303	—	—	—	—	-3·94	-6·91	-3·88	-6·79	—	—
	18315	—	—	—	—	-4·16	-6·71	—	—	—	—
	18339	—	—	—	—	-4·20	-7·16	—	—	—	—
CLYDACH BEDS	18335	—	—	—	—	—	—	-1·65	-5·10	—	—
BLAEN ONNEU OOLITE	17841	+0·56	-5·86	—	—	—	—	+0·45	-5·56	—	—
	17872	—	—	—	—	-3·04	-7·04	—	—	—	—
	17899	—	—	—	—	-4·84	-6·83	—	—	—	—
	17902	—	—	—	—	-3·46	-6·87	—	—	—	—
	18349	—	—	—	—	—	—	-3·31	-7·12	—	—
	20542	—	—	—	—	—	—	-0·28	-6·19	—	—
DAREN DDÛ BEDS	17879	—	—	—	—	—	—	+0·67	-6·26	—	—
								+2·23	-6·13		
PWLL-Y-CWM OOLITE	17829	-0·57	-8·87	—	—	—	—	+2·51	-5·07	—	—
	17830	+1·95	-5·95	—	—	—	—	+0·79	-9·67	—	—
	17834	+1·57	-5·59	—	—	—	—	—	—	—	—
	17843	-0·95	-6·71	—	—	—	—	—	—	—	—
	17869	-1·04	-7·01	—	—	—	—	+4·46	-4·63	—	—
	17875	-1·63	-7·23	—	—	—	—	—	—	—	—
	17878	-1·73	-7·01	—	—	—	—	-1·15	-8·47	—	—
	17905	—	—	-2·56	-6·78	—	—	—	—	—	—

Fig.7/1 $\delta^{13}C$ AND $\delta^{18}O$ COMPOSITION OF ALLOCHEMS

Table of $\delta^{13}C$ and $\delta^{18}O$ values obtained from allochems from the Oolite Group.

Fig.7/2 $\delta^{13}C$ AND $\delta^{18}O$ COMPOSITION OF ALLOCHEMS

Graphs of the $\delta^{13}C$ and $\delta^{18}O$ values obtained from allochems from the Oolite Group.

a)From the Gilwern Oolite(squares)

b)From the Clydach Beds(crosses)

c)From the Blaen Onneu Oolite and the Daren Ddu Beds(circles)

d)From the Pwll-y-cwm Oolite(triangles)

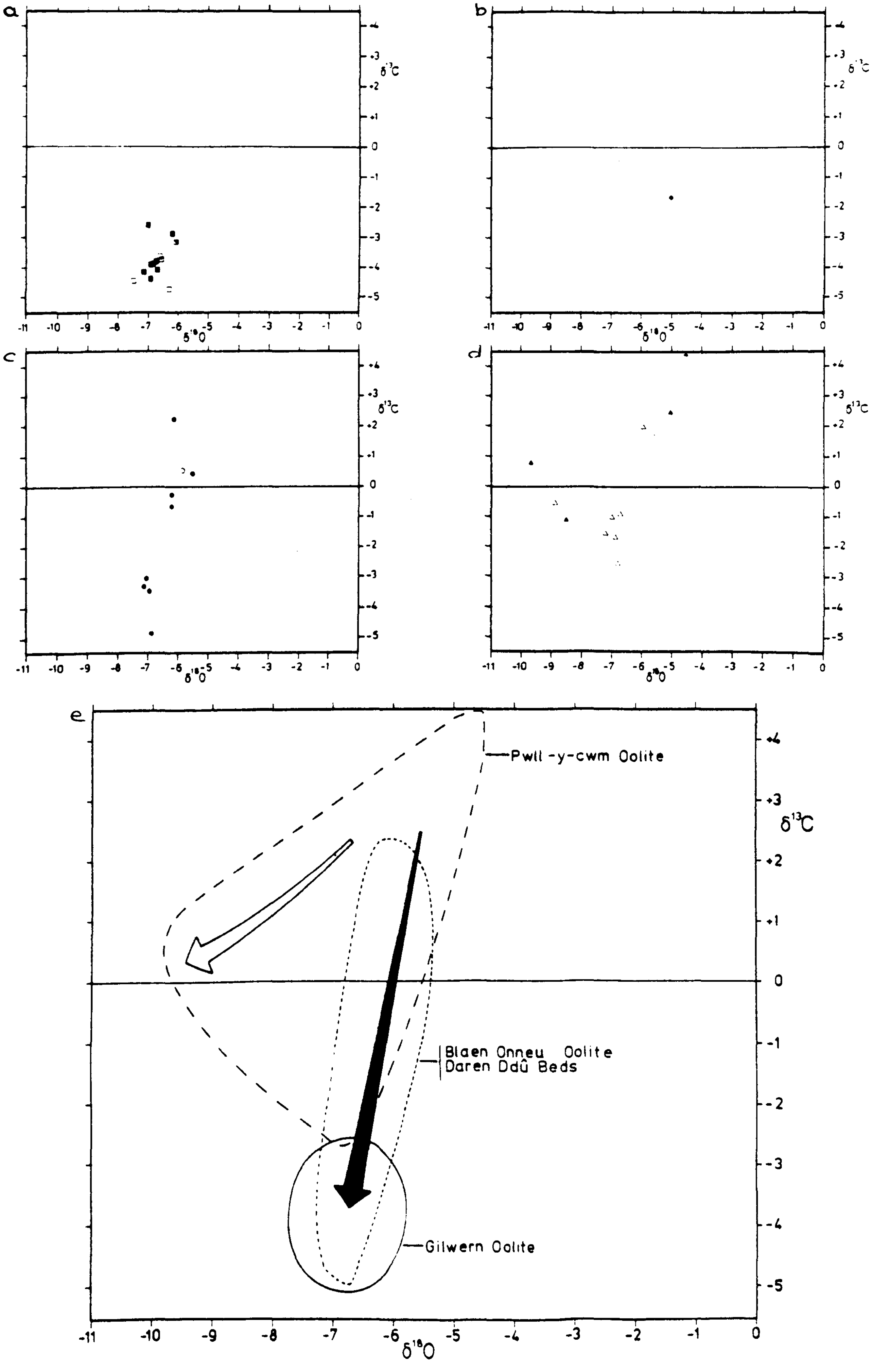
(solid symbols - brachiopods;open circles - ooids;half filled symbols - crinoid ossicles)

e)Comparison of the fields in which allochems from the various Oolite Group members lie.Two trends are evident:

1)to decreasing $\delta^{13}C$ values(solid arrow)

2)to decreasing $\delta^{13}C$ and $\delta^{18}O$(open arrow)

The latter trend is only seen in the Pwll-y-cwm Oolite.


a
b
c
d
e
δ¹³C
δ¹⁸O
Pwll-y-cwm Oolite
Blaen Onneu Oolite
Daren Ddû Beds
Gilwern Oolite

Discussion

Carbon

Fig. 7/3 shows the relationship between $\delta^{13}C$ and the depth below the exposure surface at the top of the Oolite Group. No attempt has been made to draw a line through this data since there is a possible error in some of the 'depth' measurements of up to several metres which results from logged sections consisting of several discontinuous outcrops. Due to the slope of the data, small variations in this measurement will have a pronounced affect on the slope of any line(s) constructed. It is obvious, however, that there is a trend to more 'marine' $\delta^{13}C$ values with increasing depth below the exposure surface at the top of the Oolite Group. This trend covers a vertical distance of 40 m; the entire thickness of the Group. It can be explained in terms of decreasing meteoric alteration, of originally marine allochems, with depth below the exposure surface at the top of the Oolite Group.

Allan & Matthews (1977) describe a similar trend in Barbados limestone and attributed light $\delta^{13}C$ values to the equilibration of the limestones with groundwaters containing ^{12}C-enriched soil gas CO_2. It is difficult to draw a direct comparison between the Barbados limestones and those of the Oolite Group because in the former case the trend is confined to the top six or so metres below the exposure surface whereas in the Oolite Group it extends to a depth of seven times this. Logically such a trend should be confined to the vadose zone where the net transport of water is downwards and where there is a continual supply of light soil gas. In the phreatic zone the net transport direction is laterally and so there is no replenishment of light soil gas and the carbon isotopes in the water are probably in equilibrium with the

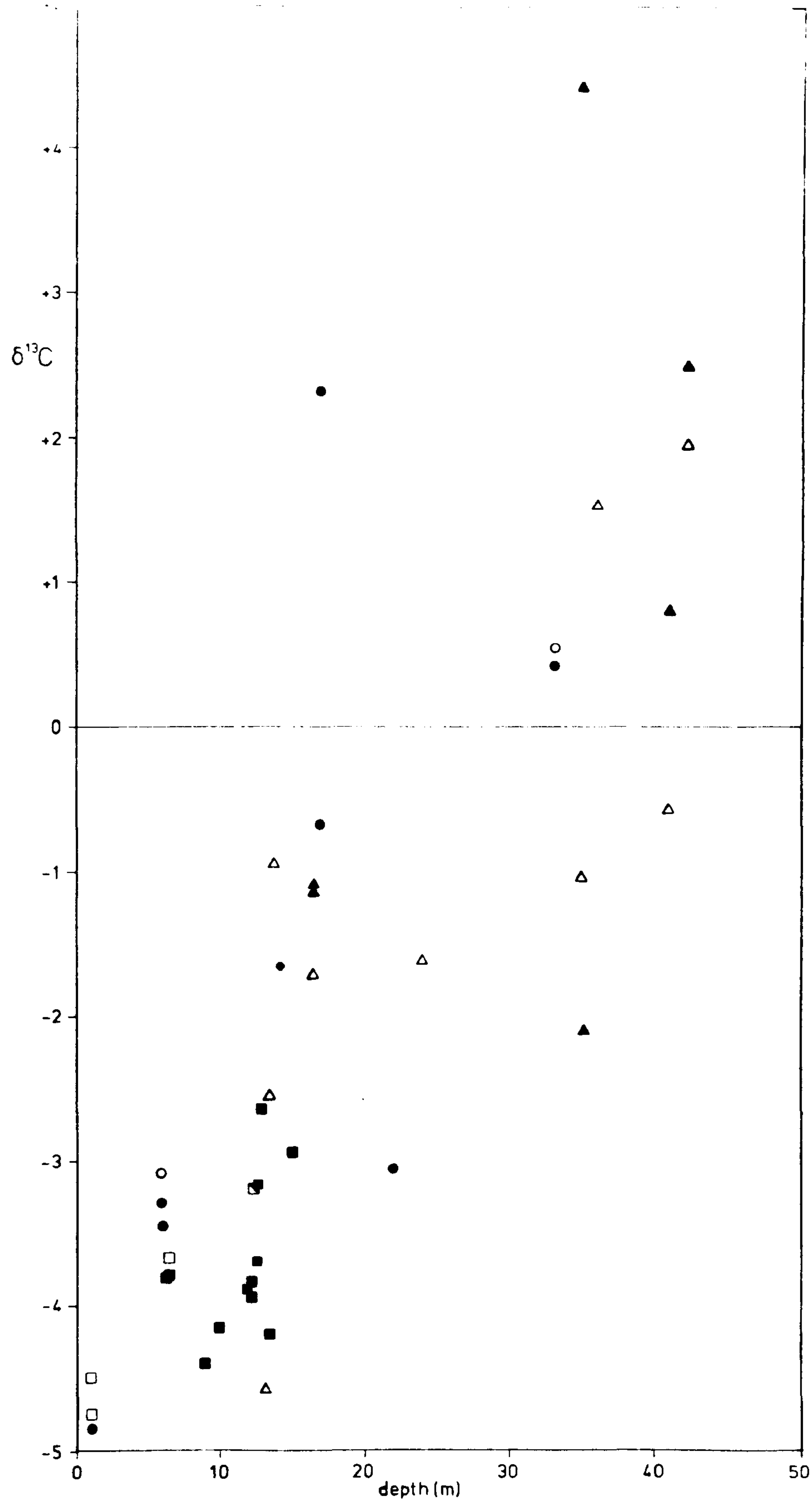


Fig.7/3 VARIATION OF $\delta^{13}C$ OF ALLOCHEMS WITH DEPTH BELOW THE TOP OF THE OOLITE GROUP

Graph of $\delta^{13}C$ v depth below the exposure surface at the top of the Oolite Group. There is a trend to heavier $\delta^{13}C$ with increasing depth. Symbols are the same as those used in Fig.7/2. Red symbols identify values from Zone 2a cements.

allochems. The evidence suggests that the water table during exposure was no more than two metres below the exposure surface (see Chapter 1). Therefore, the exact origin of the trend shown in Fig. 7/3 is in doubt although it would appear to be associated with exposure.

Marine $\delta^{13}C$ values aee only obtained from the Pwll-y-cwm and Blaen Onneu Oolites in the Clydach area, where the Oolite Group is thickest. Here numerous shale horizons occur in the Clydach and Daren Ddu Beds. These would inhibit any downward flow of meteoric water and so enhance the possibility of the preservation of original isotopic values.

Although there are a number of other exposure surfaces in the Oolite Group these seem to have had little effect on the isotopic values of the underlying allochems. This may, in part, be an artifact reflecting insufficient sampling, however there could be other explanations:

a) a soil zone was not developed during exposure and so there was no source of ^{12}C enriched CO_2 with which allochems could re-equilibrate;

b) exposure did not continue for a sufficiently long period for $\delta^{13}C$ of the allochems to be significantly altered.

Different explanations will doubtless be required for the various exposure surfaces depending on their nature. There are exposure surfaces in the overlying Llanelly Fm., the extent to which these have affected the Oolite Group is unknown.

The variation in $\delta^{13}C$ with depth partially explains the different fields in which the allochems of the different rock units fall. The allochems of the Gilwern Oolite were closest to the exposure surface; they were never more than 6 m. below it, i.e.

the maximum thickness of the Gilwern Oolite. As a result these have all completely re-equilibrated and hence fall in a tight cluster (Fig. 7/2a) at the base of the trend with a $\delta^{13}C$ = $-5^{o}/oo$. This must reflect the carbon isotopic composition of the groundwaters; heavier than the base of the trend found by Allan & Matthews (1977) which was $-10^{o}/oo$. The thinning and disappearance of the Gilwern Oolite and Clydach Beds westwards means that as one moves in that direction along the outcrop the exposure surface lies at progressively lower stratigraphic levels and so $\delta^{13}C$ values in the Pwll-y-cwm and Blaen Onneu Oolites become lighter in that direction.

Oxygen:

The narrow range of $\delta^{18}O$ observed may, like the $\delta^{13}C$ values, reflect meteoric alteration. There is a slight trend to lighter $\delta^{18}O$ values as $\delta^{13}C$ values become lighter (Fig. 7/2e). The allochems will equilibrate with the oxygen in the groundwaters more rapidly than the carbon. However, exposure was during the Arundian and at this time South Wales lay near the equator (Faller & Briden, 1978). Here one would expect precipitation with a similar $\delta^{18}O$ as seawater (Dansgaard, 1964), i.e. it would precipitate calcite with typical marine $\delta^{18}O$ values. Dickson & Coleman (1980) have also reported Arundian allochems with marine $\delta^{13}C$ but with $\delta^{18}O$ of $-6^{o}/oo$. They account for this by suggesting that either:

1. this is an original value and the allochems were precipitated in equilibrium with seawater with an isotopic composition different to that found today;
2. there has been re-equilibration of skeletal carbonate with $\delta^{18}O$ light formation waters, but not meteoric water.

Re-equilibration with meteoric water has occurred, as demonstrated by the $\delta^{13}C$ values. If the light $\delta^{18}O$ values are in equilibrium with meteoric water, as suggested by their restricted range, either a mechanism must be found by which isotopically light precipitation is formed from normal seawater or seawater had a different $\delta^{18}O$ during the Arundian than it does today. It seems unlikely that two periods of re-equilibration occurred, one with meteoric water which caused the light $\delta^{13}C$ values and the other with water of unknown origin that produced light $\delta^{18}O$ values but left $\delta^{13}C$ unchanged.

Secular changes in the $\delta^{18}O$ of seawater were suggested by Brand & Veizer (1981). They suggested that Mississippian seawater lay in the range -3 to 0^{o}/oo. Brand (1982) suggested a range of +0.5 to -3.5^{o}/oo from the study of Carboniferous fossils which included original aragonite molluscs. The values of $\delta^{18}O$ in the Oolite Group are approx. 3^{o}/oo lighter than the lower limit of these ranges. Although one would expect precipitation at the equator to have the same $\delta^{18}O$ value as seawater, seasonal weather patterns mean that a range of values are observed. The following figures are taken from Dansgaard (1964) and are values for oceanic islands and coastal towns near the equator.

	LATITUDE	$\delta^{18}O$ ISOTOPIC COMP. OF PRECIPITATION
St. Tomé Is.	0^{o}	0 - -4^{o}/oo
Hollandia	3^{o}S	-3 - -9^{o}/oo
Seychelles	4^{o}S	+4 - -8^{o}/oo
Hawaii	2^{o}N	-1 - -4^{o}/oo
Canton Is.	3^{o}S	+2 - -3^{o}/oo

Considering the size of the variation shown above it does not seem unreasonable to presume that although South Wales lay near the equator in the Arundian the mean $\delta^{18}O$ of the precipitation was slightly lighter than seawater. This, accompanied by the secular change in $\delta^{18}O$, could explain the values of $\delta^{18}O$ observed. Hence, only one re-equilibration event would be needed to account for the observed isotopic values.

In the Clydach area the Pwll-y-cwm Oolite allochems show a shift to lighter oxygen values (Fig. 7/2e). A similar trend is shown in the associated cements (Fig. 7/7a). This is probably the result of later re-equilibration.

'Ferroan' ooids from sample 17844 have $\delta^{18}O$ that is $1.2^{o}/oo$ lighter than unaltered ooids. This is consistent with attributing their ferroan hue to dissolution and precipitation of Zone 6 calcite in the resulting voids. Zone 6 calcite has considerably lighter oxygen values than allochems. This would require the re-equilibration of the allochems prior to Zone 6 precipitation. This is consistent with the petrographic evidence that shows Zone 6 cements to post-date exposure at the top of the Oolite Group.

Re-equilibration may have destroyed isotopic variations established during sedimentation or as a result of early diagenesis. For instance, variations in the original minerallogy and perhaps isotopic composition are not reflected in the isotopic values seen now. Did such variations ever exist? Ooids from above and below the exposure surface in sample 17856 have almost identical isotopic values despite their differing internal structure and diagenetic histories. Were they always the same?

7.3 Cements

Sample Descriptions

A cement zonation scheme was set up in 2.3. The first order zones that were identified were separated and analysed. Since sampling is done from stained thin sections it is impossible to separate second and third order zones as these can only be identified with CL and in any case they would usually be too small to separate in their own right. Any isotopic variation between second and third order zones is lost in the sampling process. The isotopic values obtained for the first order zones will be an average of the isotopic composition of the entire zone. Unless the variations between second and third order zones are small it will be meaningless to relate $\delta^{18}O$ and $\delta^{13}C$ values obtained to the precipitating fluids. This problem is particularly acute for samples similar to those of Zone 5 where it consists of alternating ferroan and non-ferroan calcite.

Zones 3 and 5 are subject to the largest sampling errors since they are usually very small. Therefore these will contain an appreciable amount of material from adjacent zones.

Results

The results of the analysis of the cements are presented in Figs. 7/4, 5, 6 and 7. Samples that show typical zonation are separated from those which show unusual cement types. Many of the Zone 6 cements sampled show 'Fir-tree' zonation. The two ferroan calcites comprising this zonation pattern were separated and are indicated by brackets in Fig. 7/4. Where Zone 6 shows 'normal' growth zonation (sample 17856) these zones were separated.

It can be seen from the figures that the cement zones show no progressive trend. However, the same consecutive zones in different

Fig.7/4 $\delta^{13}C$ AND $\delta^{18}O$ COMPOSITION OF CEMENTS

Table of $\delta^{13}C$ and $\delta^{18}O$ values obtained from cements from the Oolite Group.The samples above the thick line show the typical cement zones,whereas those below the thick line do not fit into the zonal scheme.In samples that do not generally fit the zonal scheme(below the thick line) it is occasionally possible to correlate individual zones with those in the zonal scheme.Where this is the case the zone number with which it correlates is shown next to the value obtained from it.Where zones are present,but are too small to sample the appropriate space is filled by the words 'too small'.

POSITION	SAMPLE NO.	ZONE 1 $\delta^{13}C$	ZONE 1 $\delta^{18}O$	ZONE 2 $\delta^{13}C$	ZONE 2 $\delta^{18}O$	ZONE 3 $\delta^{13}C$	ZONE 3 $\delta^{18}O$	ZONE 4 $\delta^{13}C$	ZONE 4 $\delta^{18}O$	ZONE 5 $\delta^{13}C$	ZONE 5 $\delta^{18}O$	ZONE 6 $\delta^{13}C$	ZONE 6 $\delta^{18}O$	ZONE 7 $\delta^{13}C$	ZONE 7 $\delta^{18}O$	VEIN 1 $\delta^{13}C$	VEIN 1 $\delta^{18}O$	VEIN 2 $\delta^{13}C$	VEIN 2 $\delta^{18}O$
GILWERN OOLITE	17842	—	—	—	—	—	—	-6·18	-6·96	—	—	—	—	—	—	—	—	—	—
	17844	—	—	too	small	—	—	-5·48	-6·47	—	—	-2·75	-7·73	-3·40	-5·20	—	—	—	—
								-5·14	-6·22			-3·33	-8·74						
	(a)							-5·73	-6·75										
	(b)							-5·19	-6·17										
(Coral Bed)	17862	—	—	-3 20	-6·40	—	—	-4·74	-7·03	-3·68	-5·78	-0·05	-4·02	—	—	—	—	—	—
												-0·19	-4·67						
												-2·47	-7·21						
												-0·03	-4·07						
	18303	—	—	-3·90	-7·32	-5·27	-9·27	-4·60	-6·91	-5·12	-6·32	-2·86	-8·30	—	—	—	—	—	—
												-2·97	-7·72						
	18325	—	—	-3·78	-6·43	-4·24	-7·47	-4·38	-6·91	-4·70	-6·02	-2·96	-8·35	-3·55	-4·55	—	—	—	—
												-3·53	-9·31	-2·98	-5·09				
	(a)											-2·87	-8·41						
	(b)											-3·38	-9·11						
BLAEN ONNEU OOLITE	17902	—	—	too	small	too	small	-4·85	-6·58	—	—	-3·56	-9·11	—	—	-4·16	-8·12	—	—
												-3·76	-9·40						
	18349	—	—	-3·08	-7·66	too	small	-4·41	-7·44	too	small	-3·06	-9·77	—	—	—	—	—	—
												-3·28	-10·05						
PWLL-Y-CWM OOLITE	17829	+0·11	-7·71	-0·14	-7·93	—	—	too	small	—	—	+0·60	-11·52	—	—	—	—	—	—
	17830	+0·59	-7·50	-0·51	-9·05	—	—	too	small	—	—	+1·31	-11·14	—	—	—	—	—	—
	17869	too	small	-2·12	-8·28	-5·45	-10·36	-4·14	-8·80	-5·40	-9·97	-1·97	-7·49	—	—	-0·87	-13·96	-0·43	-14·86
	17878	—	—	-1·12	-5·34	-6·02	-11·13	-4·28	-7·70	too	small	-2·51	-11·14	—	—	-2·36	-9·55	—	—
												-2·59	-11·05						
	17905	—	—	-4·59	-8·47	—	—	-4·16	-6·23	—	—	-3·69	-10·36	—	—	-2·53	-11·46	—	—
								-4·60	-6·95										
GILWERN OOLITE	17856	—	—	—	—	-4·76	-6·85[4/5]	-3·61	-5·56	-3·98	-5·94	-3·22	-11·96[6]	—	—	—	—	—	—
	20592	—	—	—	—	—	—	—	—	—	—	-4·02	-12·01[6]	—	—	—	—	—	—
CLYDACH BEDS	18335	—	—	too	small	-4·58	-8·13	+0·23	-5·21[6]	—	—	—	—	—	—	—	—	—	—
DAREN DDÛ BEDS	17879	-5·69	-12·35	-5·38	-7·93	too	small	—	—	—	—	-2·48	-9·99[6]	—	—	-1·28	-13·61	-0·03	-16 86
	17886	—	—	-4·95	-8·78	-4·66	-9·70	-5·20	-8·28[4]	too	small	-4·70	-8·31[5]	—	—	-4·86	-7·70	—	—
	(b)											-3·28	-12·14[6]						

Fig.7/5 $\delta^{13}C$ AND $\delta^{18}O$ COMPOSITION OF CEMENTS FROM THE GILWERN OOLITE

Graphs of the $\delta^{13}C$ and $\delta^{18}O$ values obtained from cements from the Gilwern Oolite.

a)Samples showing typical zonation,from above the Coral Bed.

b)Samples showing atypical zonation,from above the Coral Bed.

c)Samples showing typical zonation,from the Coral Bed.

The numbers correspond to the zonal numbers shown in the table in Fig.7/4. In the case of (a) and (c) these also correspond to the zones of the typical zonation scheme.Adjacent samples are connected to show the variation in the isotopic composition of the cements with time.(solid symbols - cement zones; open symbols - associated allochems)

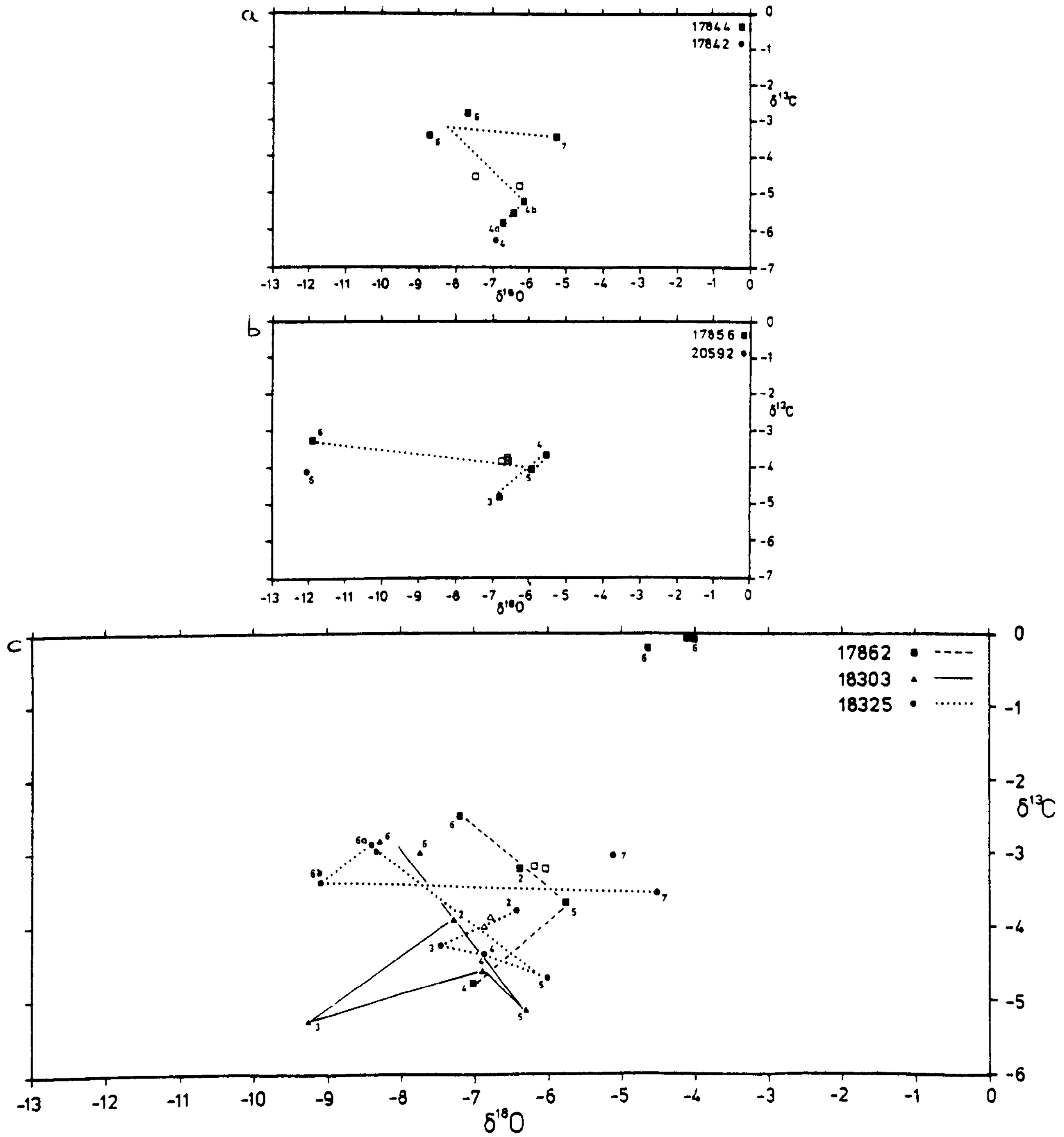

a
17844
17842
δ13C
δ18O
b
17856
20592
δ13C
δ18O
c
17862
18303
18325
δ13C
δ18O

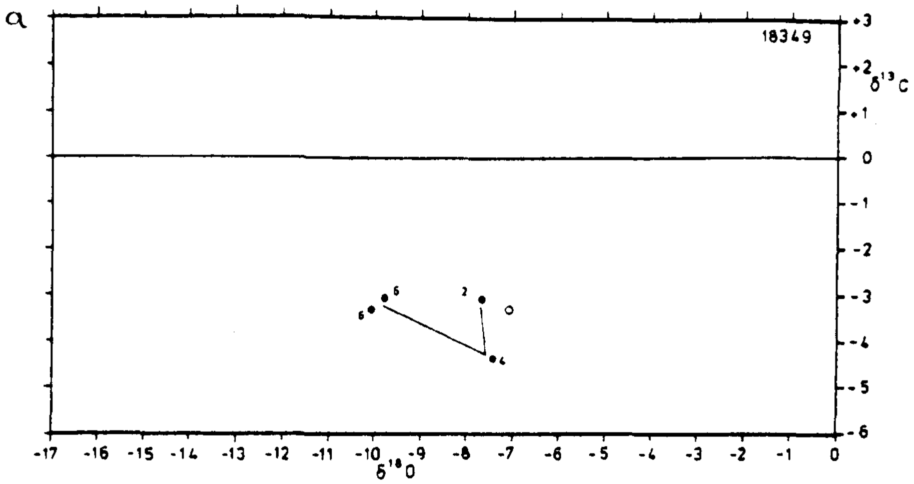
Fig.7/6 $\delta^{13}C$ AND $\delta^{18}O$ COMPOSITION OF CEMENTS FROM THE BLAEN ONNEU OOLITE AND THE DAREN DDU BEDS

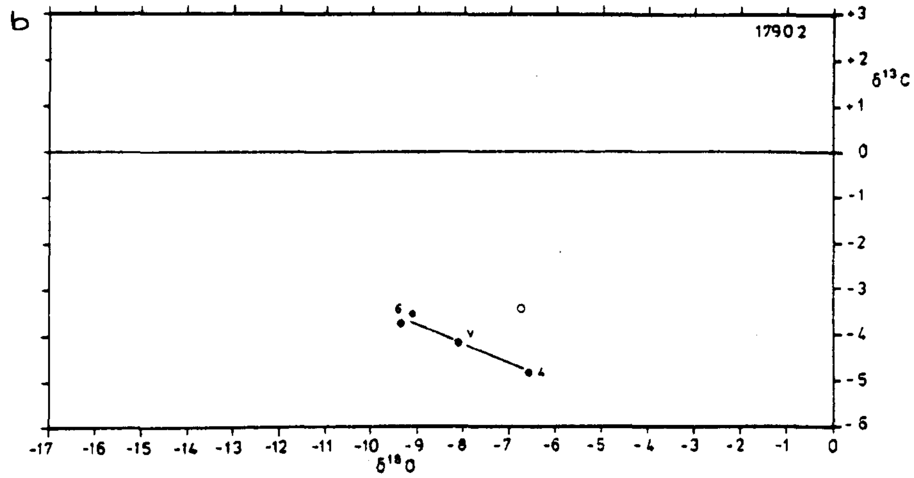
Graphs of the $\delta^{13}C$ and $\delta^{18}O$ values obtained from cements from the Blaen Onneu Oolite and the Daren Ddu Beds.

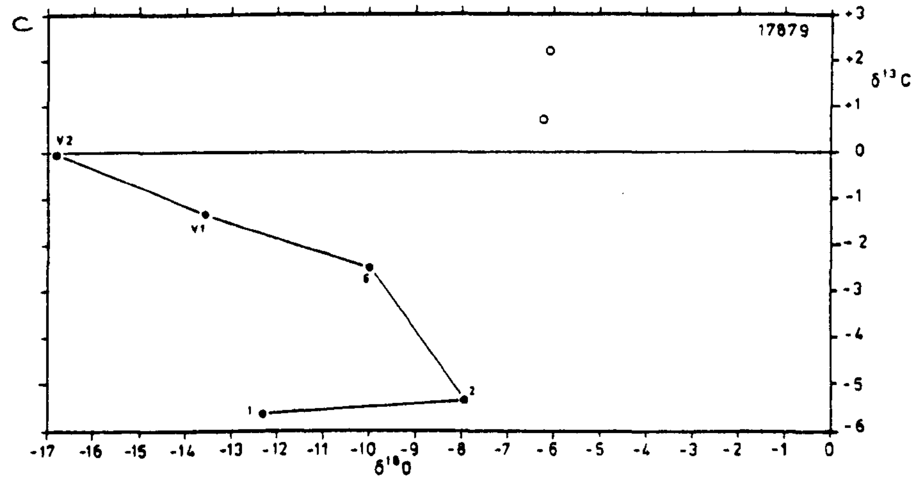
a) and (b) Samples showing typical zonation from the Blaen Onneu Oolite.

c) and (d) Samples showing atypical zonation from the Daren Ddu Beds.

The numbers correspond to the zonal numbers shown in the table in Fig.7/4. In the case of (a) and (b) these also correspond to the zones of the typical zonation scheme. Adjacent samples are connected to show the variation in the isotopic composition of the cements with time. (solid symbols - cement zones; open symbols - associated allochems; v - veins)


a
18349
δ13C
δ18O


b
17902
δ13C
δ18O


c
17879
δ13C
δ18O

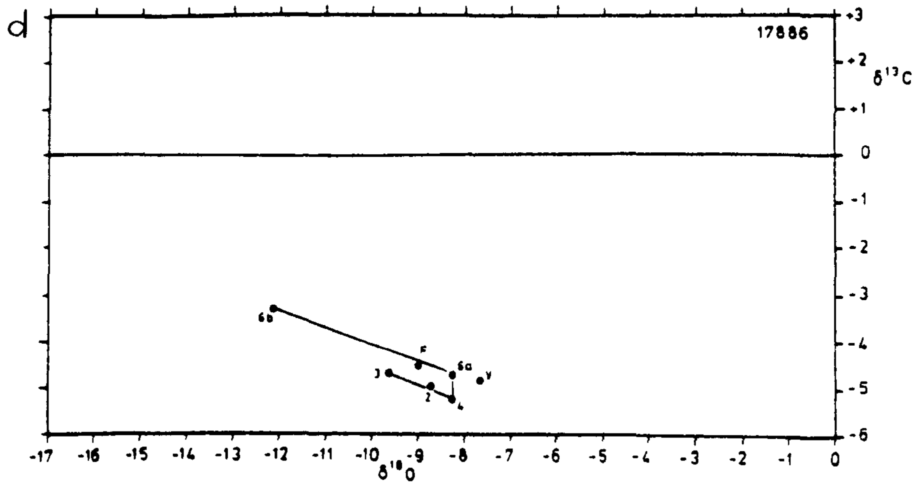

d
17886
δ13C
δ18O

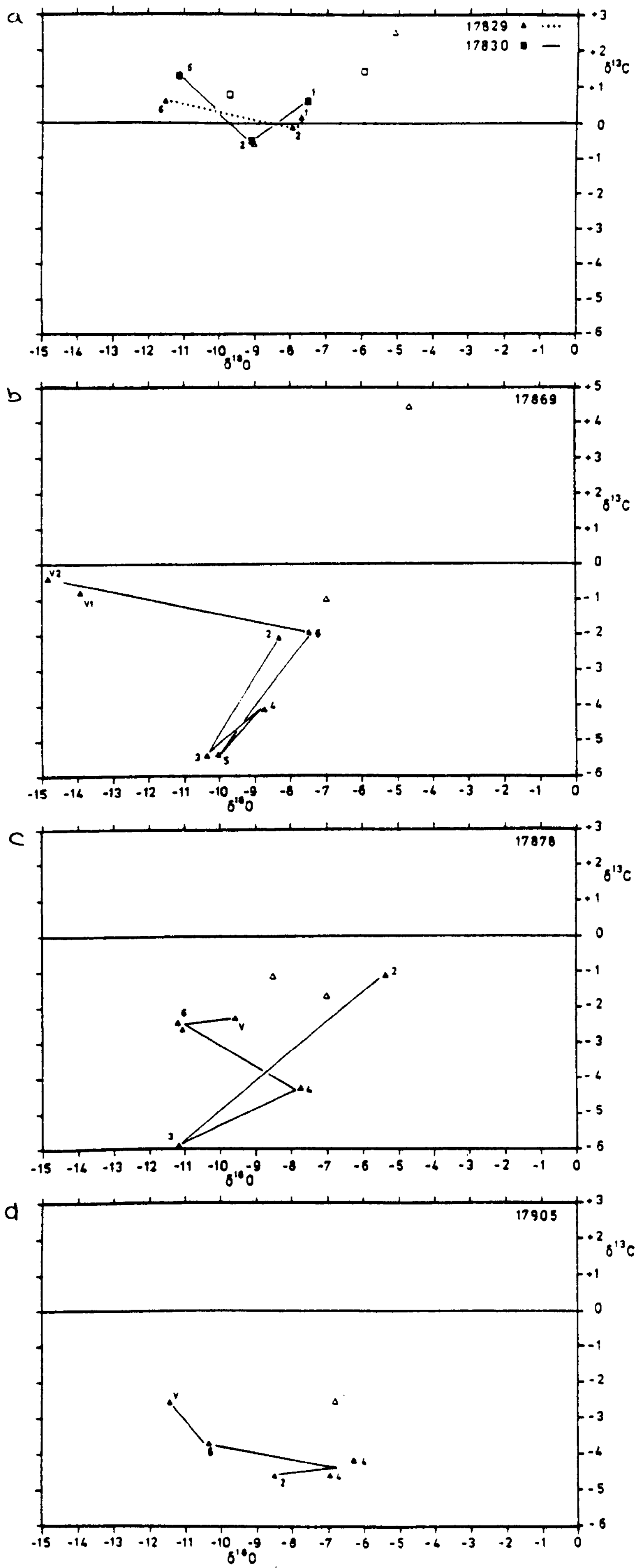
Fig.7/7 $\delta^{13}C$ AND $\delta^{18}O$ COMPOSITION OF CEMENTS FROM THE PWLL-Y-CWM OOLITE

Graphs of the $\delta^{13}C$ and $\delta^{18}O$ values obtained from cements from the Pwll-y-cwm Oolite.

a)Samples showing typical zonation from Diagenetic Area 1.

b)-(c)Samples showing typical zonation from Diagenetic Area 2.

The numbers correspond to the zonal numbers shown in the table in Fig.7/4. These all correspond to the zones in the typical zonation scheme.Adjacent samples are connected to show the variation in the isotopic composition of the cements with time.(solid symbols - cement zones;open symbols - associated allochems;v:- veins)


a
17829
17830
δ13C
δ18O
b
17869
δ13C
δ18O
c
17878
δ13C
δ18O
d
17905
δ13C
δ18O

samples do have similar relative isotopic values. These are summarised in Fig. 7/8. Not surprisingly the cements that do not fit into the zonation scheme do not conform to these changes. The cements of the Pwll-y-cwm Oolite in the Clydach area, where it consists of Zones 1, 2b and 6, lie in a position away from the rest of the cements. This is rather surprising.

Discussion

The cements that show the usual zonation pattern (Zones 2a, 3, 4, 5, 6 and 7) will be considered first, then the cements from the Pwll-y-cwm Oolite showing Zones 1, 2b and 6. Finally the cements that do not fit into the zonation pattern and veins will be considered.

Cements showing the typical zonation pattern

Fig. 7/8 shows that each zone has a distinct range of values associated with it. That this is the case confirms the validity of the zonation scheme that has been constructed and the ability of the author to distinguish these zones in different samples. Variations in the isotopic composition of zones reflects variations in the isotopic composition of the pore fluids from which they were precipitated. The values of each of the zones is considered in more detail below.

Zone 2a - it was established in 2.1 that Zone 2a cements were 'early' and probably marine. Their present isotopic values do not reflect a marine origin. Since they are 'early' they should have re-equilibrated, along with the allochems, during exposure of the top of the Oolite Group. This and the solutions features that are ubiquitous in Zone 2a cements (Chapter 3) means that it is extremely unlikely that they retain their original isotopic composition. Examination of Figures 7/5c, 6a and 7b, c, d show

Fig.7/8 $\delta^{13}C$ AND $\delta^{18}O$ COMPOSITION OF CEMENTS WITH A TYPICAL ZONATION PATTERN

Graph of the $\delta^{13}C$ and $\delta^{18}O$ values obtained from cements showing the typical zonation pattern.The shape of the symbols identifies which member the sample originates from(square - Gilwern Oolite;cross - Clydach Beds;circle - Blaen Onnen Oolite and Daren Ddu Beds;triangle - Pwll-y-cwm Oolite).The various cement zones are identified as follows:

Zone 1 - top half filled

Zone 2a- open with a dot

Zone 2b- green

Zone 3 - left half solid

Zone 4 - open

Zone 5 - right half solid

Zone 6 - solid

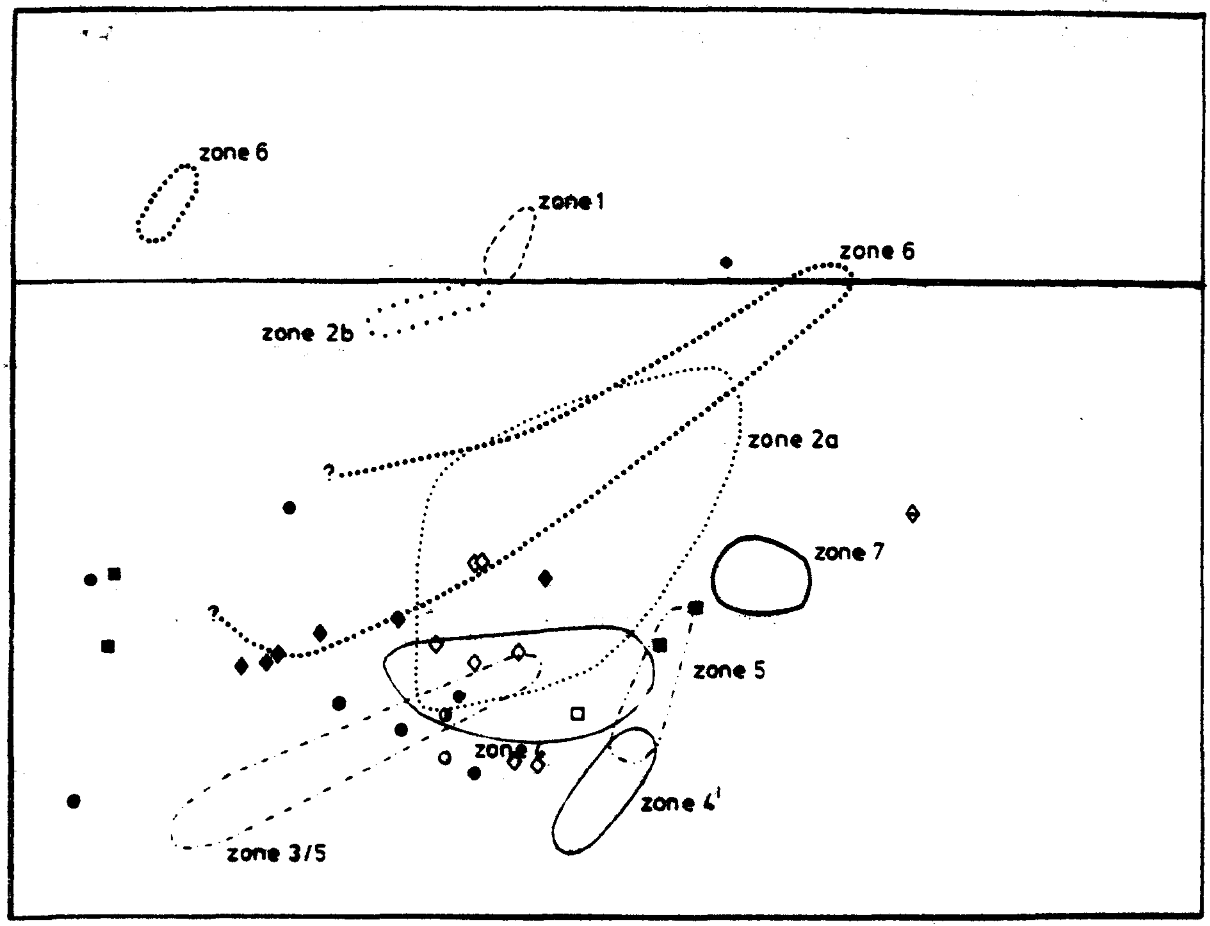
Zone 7 - open with horizontal line

Overlay 1

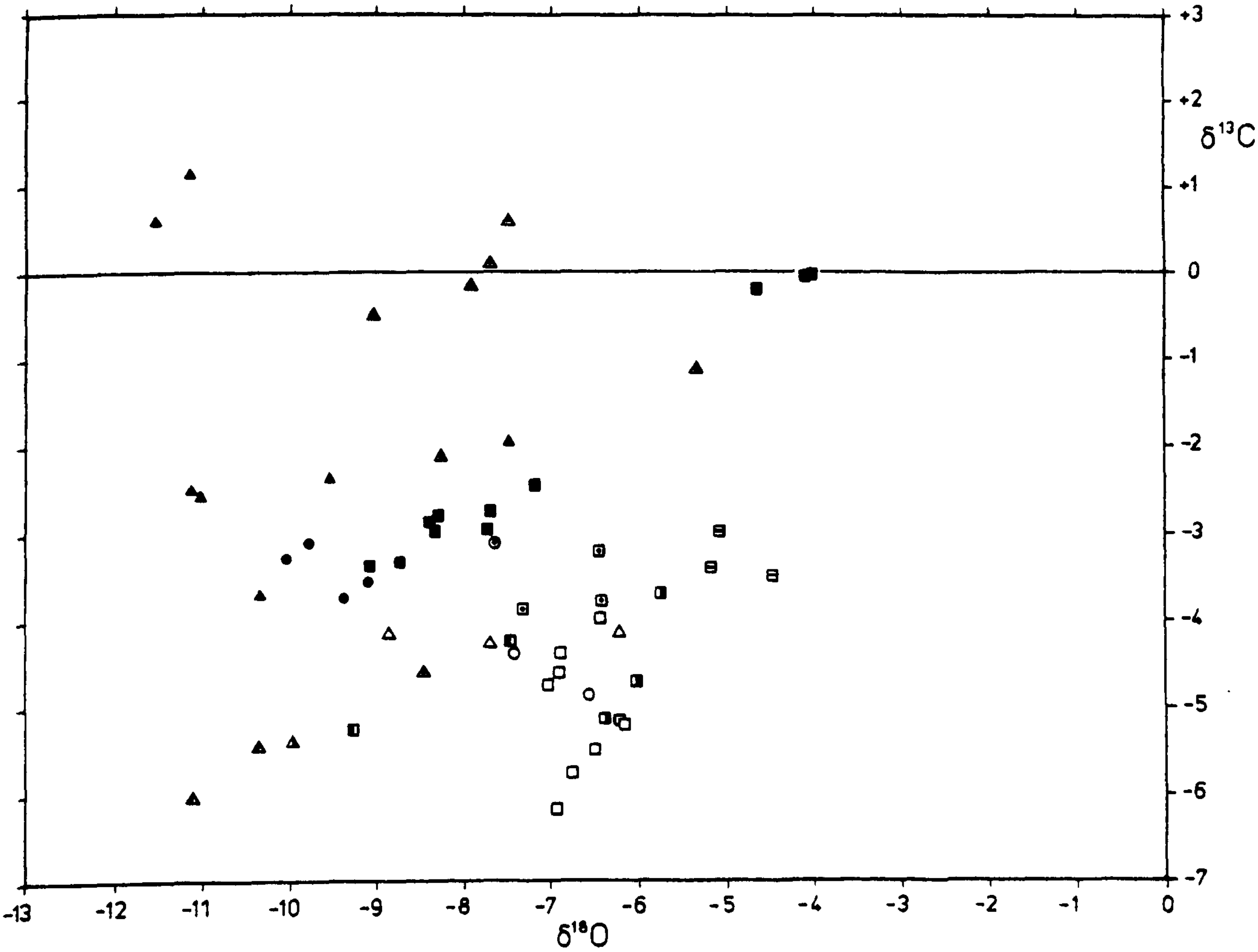
The various fields into which the cement zones fall are outlined.Zone 4 has been divided into two.The 'early' Zone 4 cements from the top of the Gilwern Oolite are separated from the rest and are identified as Zone 4'.

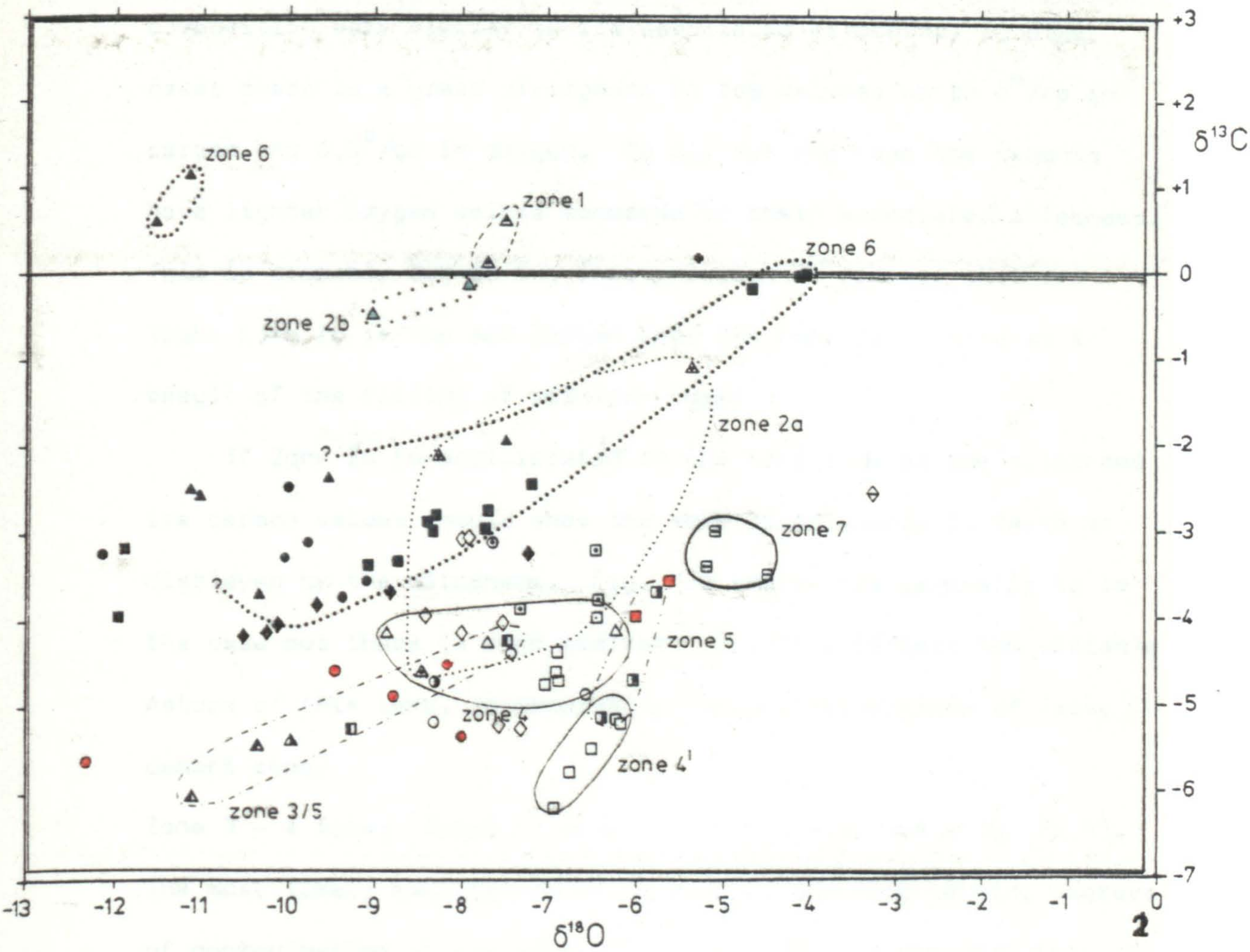
Overlay 2

The samples that do not show the typical zonation pattern are plotted.Where zones possibly correlate with the normal zonation scheme this is indicated by the use of the symbols listed above.Zones that do not fit into the zonation scheme are coloured red. Also shown are calcite cements from concretions - diamonds.


zone 6
zone 1
zone 6
zone 2b
zone 2a
zone 7
zone 5
zone 4
zone 4'
zone 3/5

2


+3
+2
+1
0
-1
-2
-3
-4
-5
-6
-7
δ13C
-13
-12
-11
-10
-9
-8
-7
-6
-5
-4
-3
-2
-1
0
δ18O


zone 6
zone 1
zone 6
zone 2b
zone 2a
zone 7
zone 5
zone 4
zone 4'
zone 3/5
?
?
+3
+2
+1
0
-1
-2
-3
-4
-5
-6
-7
δ13C
-13
-12
-11
-10
-9
-8
-7
-6
-5
-4
-3
-2
-1
0
δ18O
2

that although in some cases Zone 2a cement has an isotopic composition very similar to its associated allochems, in other cases there is a great divergence in the values; up to $6^{o}/oo$ in carbon and $3.5^{o}/oo$ in oxygen. In all but one case the cements have lighter oxygen values compared to their associated allochems. This is probably due to the incorporation of cements that are light both in carbon and oxygen into the Zone 2a calcite as a result of the filling of solution vugs.

If Zone 2a re-equilibrated at the same time as the allochems its carbon values should show the same relationship to depth as displayed by the allochems. Fig. 7/3 shows this generally to be the case but there is much scatter. This may reflect the variable nature of this zone, incorporating varying proportions of later cement zones.

Zone 3 - a linear trend is shown by Zone 3 calcites (Fig. 7/ 8). The most likely explanation of this is by assuming varying degrees of contamination of the samples by Zone 2a and 4 cements, both of which lie at the heavy end of the trend. Values obtained from samples 17869 and 17878 fall at the lighter end of the trend. These are known to be the purest of the Zone 3 samples, which is consistent with them lying furthest from the Zone 2a and 4 values. The values obtained from these two samples are probably the most representative of the pore fluids that precipitated Zone 3 calcite.

It is difficult to interpret the isotopic values of this zone, $\delta^{13}C = -6^{o}/oo$, $\delta^{18}O = -11^{o}/oo$. The value of $\delta^{13}C$ is only slightly lighter than that of allochems re-quilibrated with meteoric groundwaters. So the origin of the carbon isotopic values may be due to the presence of light soil gas CO_2. Some of the problems associated with interpreting $\delta^{18}O$ values have already been discussed in 7.2. The origin of a $\delta^{18}O = -11^{o}/oo$ is by no means clear. Meteoric derived fluids would be expected to be at least $5^{o}/oo$ heavier than this since Zone 3 is probably 'early'. Zone 4 - Zone 4a cements that are associated with the exposure of the top of the Oolite Group fall in a group distinct from the rest of the Zone 4 samples. These have lighter carbon and heavier oxygen values (Fig. 7/8). These 'early' cements fall at the extreme end of the trend illustrated in Fig. 7/3. Precipitation from ^{12}C-enriched soil gas CO_2 seems to be their most likely origin.

Other Zone 4 calcites that are from closely related samples, e.g. those of the Coral Bed, fall in a tight cluster (Fig. 7/5c), but Zone 4 calcites from unrelated samples show a wider scatter of values (Fig. 7/8). It was pointed out in 2.3 that there is a lateral variation in the second order zones present in Zone 4 calcites and the variations in their isotopic values may reflect this.

The mean value of 'late' Zone 4 cements is $\delta^{13}C = -5.5^{o}/oo$, $\delta^{18}O = -7.5^{o}/oo$. The same problems exist in interpreting these values as was discussed in the case of Zone 3. However, these cements are known to be 'late', although their precise age is uncertain. This means that they could have been precipitated when South Wales was at a higher latitude; in which case meteoric waters would be lighter. However, this would mean that they were precipitated many tens, even hundreds, of millions of years after the deposition of the Oolite Group.

Zone 5 - the isotopic values found for Zone 5 cements depend on whether it consists of a single ferroan zone or alternating ferroan and non-ferroan second order zones. In the latter case Zone 5 lies to the right (heavier oxygen) of Zone 4 (Figs. 7/5c and 8). There is likely to be contamination from both Zone 4 and 6 cements so the $\delta^{18}O$ values obtained will be a minimum value.

In samples where Zone 5 consists of a single ferroan zone (17869 is the only sample in which this could be separated) it lies within the field of Zone 3 (Figs. 7/7c and 8). This suggests a similarity of the source fluids of Zones 3 and 5 ferroan calcites.

Isotopic variations may well exist within Zone 5 cements consisting of a number of ferroan and non-ferroan second order zones, but these will be masked by the sampling technique. The interpretation of the values obtained from such samples is meaningless in terms of the isotopic composition of the precipitating fluids.

The same problems exist in interpreting the isotopic values of Zone 5 calcites as has been discussed for Zones 3 and 4. The $\delta^{18}O$ of Zones 3-5 cannot be explained in terms of increasing temperature associated with burial as there is no consistent trend to lighter oxygen values. The temperature changes that are needed to explain the isotopic variations between Zones 3-5 are of the order of 20 - 25^{o}C, which represents a depth of up to nearly a kilometre. It is unlikely that repeated fluctuations in the depth of burial on this scale occurred. Since these variations are associated with changes in chemistry a more likely explanation is that a number of isotopically distinct pore fluids were responsible for the precipitation of the zones. Some of these cements are known to have been precipitated after the deposition of the Llanelly Fm., so may have been precipitated from pore fluids that collected when South Wales was at a higher latitude, where precipitation would have a lighter $\delta^{18}O$ value (Dansgaard, 1964).

Since most of the Oolite Group re-equilibrated with groundwaters containing light carbon early in its diagenetic history the isotopic composition of later fluids with light carbon passing through will not be affected. Fluids such as these can never have passed through sediments which retained their marine isotopic values as they would quickly re-equilibrate with this marine carbonate.

Zone 6 - the values of Zone 6 calcite fall along or to the left of a line with sample 17862 at one extreme and separated from the rest of the results and sample 17905 at the other (Fig. 7/ 8). Although 17862 is removed from the rest it does fall on the line which suggests that is not the result of analytical error. Resampling of 17862 produced results that fell both with the earlier results and within the mass of the other results from Zone 6 (Fig. 7/5c); this is not understood. The trend seen can be explained in two ways:

a) mixing between two isotopically distinct water bodies, one precipitating calcite with $\delta^{13}C = -4^{o}/oo$, $\delta^{18}O = -10.5^{o}/oo$ and the other with $\delta^{13}C = 0^{o}/oo$, $\delta^{18}O = -4.5^{o}/oo$. The heavier calcites have carbon values approaching that of marine carbonate and heavier oxygen than any other cements which also suggests a marine origin. There is evidence of an influx of sulphate-rich pore water prior to Zone 6 precipitation. Marine water would be a suitable source of this. The lighter water has isotopic values similar to those of Zone 3-5 cements, the origin of which has already been discussed.

It is odd that the crystallography and presumably the chemistry of Zone 6 cements should be so constant despite variations in the source and doubtless the chemistry of the precipitating fluids;

b) varying degrees of re-equilibration of a fluid precipitating calcite with $\delta^{18}O = -10.5^{o}/oo$, $\delta^{13}C = -4^{o}/oo$ with marine carbonate. This would require only one pore fluid and a substrate of varying isotopic composition. This suggestion is more in keeping with the constancy of the chemistry and crystallography of the cements.

Solution prior to the precipitation of Zone 5 (Solution Event 4) cement marks a major break in the precipitation history of the cements. Solution must have occurred at a shallow depth since clastic diagenetic sediment was washed in at a similar time. The depth at which Zone 6 was precipitated is unknown. The bulk of Zone 6 samples have $\delta^{18}O$ slightly lighter than Zone 3-5 cements. This may reflect a slight increase in temperature associated with increasing depth of burial. The scatter of values to the left of the line of the Zone 6 values may also be due to later precipitation of Zone 6 calcite at slightly greater depth and temperature.

Zone 7 - there is no consensus as to the fractionation factor of $^{18}\alpha$ between calcite and dolomite. Estimates vary from 0-7^{o}/oo at 25^{o}C, these being based both on experiment (Northrop & Clayton, 1966; O'Niel & Epstein, 1966; Sheppard & Schwartz, 1970) and examination of recent and ancient calcite-dolomite pairs (Degens & Epstein, 1964; Freidman & Hall, 1963; Fritz, 1967). Land (1980) plumps for a value of $3\pm 1^{o}/oo$ (at 25^{o}C) for the fractionation factor.

The baroque dolomite of Zone 7 has heavier oxygen than any of the calcite cements. It is approx. 5°/oo heavier than the Zone 6 calcite that preceeds it. This value does fall within the range of suggested fractionation factors. Radke & Mathis (1980) suggest that dolomite of this type precipitates between 60 and 150°C. With increasing temperature the fractionation factor between calcite and dolomite decreases. Using the expression given by Matthews & Katz (1977), if the fractionation factor at 25°C is 3°/oo at 60°C it is 2.3°/oo and at 150°C it is 1.4°/oo. Even accepting the possibility of a higher fractionation factor at 25°C the difference of 5°/oo that is observed will be at the upper limit of the acceptable range of fractionation factors at the temperatures suggested for the precipitation of Zone 7 dolomites.

Zone 7 has both negative $\delta^{13}C$ and $\delta^{18}O$ which suggests that it is related to the earlier calcite cements. Due to the uncertainty in the estimates of the fractionation factor of ^{18}O between calcite and dolomite it is impossible to say whether the heavier oxygen values of the dolomite are purely the result of fractionation effects. If one assumes a temperature of precipitation within the range suggested by Radke & Mathis (1980), the 5°/oo difference between the dolomite and the preceeding calcite lies at the very upper limit of the acceptable range. Since Zones 6 and 7 did not co-precipitate it is not strictly correct to compare them. The shift from calcite to dolomite precipitation must reflect a change in the pore water chemistry (addition of Mg^{2+}), this may well be accompanied by a change in the isotopic composition of the pore water as well.

Cements showing Zones 1, 2b and 6

The individuality of the cements from the Pwll-y-cwm and Blaen Onneu Oolites from the Clydach area was pointed out in 2.3. This individuality is also reflected in their isotopic composition which is quite distinct from those of the rest of the Oolite Group cements.

The carbon values of the cements are small positive and negative values, typical of those one would expect from precipitation from marine water and are closely associated with the values obtained from the allochems (Fig. 7/7a). The oxygen values, however, are similar to those found in the rest of the cements. There is a trend to lighter oxygen with time.

Zone 1 cement is strongly ferroan so must have precipitated from water low in sulphate in reducing conditions. This suggests that the pore fluids were non-marine in origin. The marine, carbon isotope values could have resulted from re-equilibration of meteoric water with marine carbon from the allochems. It was stated in 7.2 that the carbon isotopic composition of meteoric groundwaters will rapidly re-equilibrate with the carbon of marine allochems. Since this portion of the Oolite Group never lost its marine carbon identity during the exposure of the top of the Oolite Group (Fig. 7/3) and later pore fluids passing through it which have light carbon isotopic compositions will tend to lose their carbon isotopic identity and take on marine values.

Atypical cements

The zone numbers shown in Fig. 7/4 for the atypical cements do not signify their position in the zonal scheme. In most of the cases the atypical cements do not fit into this scheme. The zone numbers refer to the zones that can be identified in thin section and should not be correlated with the zones of the general scheme that is outlined in 2.3. Any correlations that can be made are pointed out in the discussion below.

Discussion

Gilwern Oolite

For sample 17856 the zones numbered 3 and 4–6 in Fig. 7/4 can be correlated with Zones 4–5 and 6, respectively, of the general zonal scheme. In this sample, Zone 6 cements, of the general scheme, show 'normal' growth zonation consisting of alternating ferroan and non-ferroan calcite and are illustrated in Fig. 2/15a, b. This sample is one of several from the eastern portion of the Gilwern Oolite that shows such a zonation pattern (shaded areas in Fig. 2/23b). It was stated in 2.3 that the relationship between these and other Zone 6 cements was unclear. The isotopic composition of the two earliest Zone 6 samples is similar to associated Zone 4–5 cements (Fig. 7/5a, b) rather than typical Zone 6 values. This suggests that they pre-date the precipitation of the bulk of the Zone 6 cement and represent a limited area of precipitation after Zone 5.

The cement from 20592 is late Zone 6 non-ferroan calcite. It has a similar value to the last Zone 6 sample from 17856. These two values lie at the extreme left hand end of the trend seen in the bulk of the Zone 6 samples (Fig. 7/8) and hence would appear to be related to typical Zone 6 cements.

Clydach Beds

Zone 3 and 4 samples of 18335 (Fig. 7/4) represent diagenetic sediment and Zone 6 cement respectively. The 'early' cement underlying the diagenetic sediment was too small to sample, but brachiopods from the same sample yielded a value of $\delta^{13}C = -1.6^{o}/oo$ $\delta^{18}O = -5.1^{o}/oo$ (Fig. 7/2b).

The value of Zone 6 calcite is similar to that from sample 17862 and confirms the validity of the results obtained from this sample. The origin of this value has already been discussed. Earlier calcite is unrelated to Zone 6 cement although the brachiopods yield a remarkably similar value. It has already been suggested that these retain part of their marine carbon character.

Daren Ddu Beds

In sample 17886 zones 2 and 3 were established to be 'early' cements in 2.1. Zones 4, 6a, 6b can be correlated with Zones 4, 5 and 6 of the zonal scheme respectively. Zone 4 is more negative than typical Zone 4 cements despite the fact that correlation was good and separation of the zone accurate. Zone 5 ferroan calcite falls exactly on the trend of other Zone 3 and 5 calcites, confirming the result obtained from Zone 5 of sample 17869.

The oxygen values of the 'early' cements are discrete, suggesting that they at least in part retain some of their initial isotopic composition. Their age would suggest that they should have re-equilibrated with groundwaters during the exposure of the top of the Oolite Group. There is no sign of this in their carbon values.

The zones found in sample 17879 are outlined and illustrated in 2.3. The age of the first two zones is unknown. The final zone can be correlated with Zone 6 of the zonal scheme. The oxygen value of the initial cement is again very hard to interpret. Its negative value cannot be explained in terms of increased temperature associated with burial as the subsequent zone is approx. $5^{o}/oo$ lighter. It must reflect the fluctuations inthe isotopic composition of the pore fluids. Although the second zone that was separated has a more usual isotopic value it does not fit any of the fields defined by the other cements. It is ferroan but lies below the field of Zone 3 and 5 cement. Zone 6 cement fits reasonably well with other Zone 6 data.

Veins

Most of the veins contain Zone 6 or younger calcite. The youngest veins have very much lighter oxygen values than any of the cements, the most extreme value being $-17^{o}/oo$ (Figs. 7/6c, 7/7b). Their carbon values are only slightly heavier than the cements. The very low oxygen values are consistent with precipitation at elevated temperatures associated with deep burial.

Using the equation of O'Niel et al (1969):

$$1000 \ln \propto_{cc-H_2O} = 2.78 \cdot 10^{6} T^{-2} - 3.39 \quad \delta_{cc} - \delta_{H_2O}$$

$\propto$ - fractionation factor

T - temperature, ^{o}K

δ_{cc} - composition of calcite on SMOW scale

δ_{H_2O} - composition of water on SMOW scale

and assuming a water composition similar to that responsible for the precipitation of Zone 4 calcite ($\delta^{18}O = 7.17^{o}/oo$) and that Zone 4 calcite precipitated at approx. $30^{o}C$ a vein with $\delta^{18}O = -14^{o}/oo$ precipitated at $73^{o}C$ and one with $\delta^{18}O = -17^{o}/oo$ precipitated at $98^{o}C$. This is approx. 1.5 and 2.25 km respectively, assuming a geothermal gradient of $30^{o}C/km$. These values are consistent with the suggested origin.

7.4 Dolomites and post-dolomite calcite

Sample descriptions

These dolomites and calcites are described in Chapter 4. Samples were scraped from stained slabs. The dolomite from sample 20565 differed slightly from the other dolomite in being slightly ferroan. It was possible to separate up to 7 zones from the samples:

Zone 1 – dolomite replacing former calcite cements and allochems

Zone 2 – sparry dolomite

Zone 3, Zone 4, Zone 5 – ferroan calcite

Zone 6, Zone 7 – calcite

Results

The results of the analyses of these zones are presented in Figs. 7/9 and 10. The variation in the isotopic composition of the dolomites and calcites is very marked. The calcites show a shift to heavier $\delta^{18}O$ and lighter $\delta^{13}C$ with time. This change is not seen in any of the cements. Sparry dolomites precipitated in veins and vugs have average isotope values of $\delta^{13}C = +0.8^{o}/oo$, $\delta^{18}O = -2.9^{o}/oo$.

Discussion

Dolomite

The $\delta^{13}C$ values of the dolimites are consistent with a marine carbonate source. Interpretation of the $\delta^{18}O$ values is more difficult for the reasons discussed earlier. Assuming an oxygen fractionation

	ZONE 1		ZONE 2		ZONE 3		ZONE 4		ZONE 5		ZONE 6		ZONE 7	
SAMPLE NO.	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$
17838	+1·77	-1·76	+0·84	-2·20	—	—	-0·05	-9·71	—	—	—	—	—	—
17848	—	—	+0·48	-3·44	—	—	—	—	—	—	—	—	—	—
17859	—	—	—	—	—	—	-1·70	-10·95	—	—	-5·03	-7·52	-7·52	-6·53
18319	+1·87	-1·59	+1·09	-3·08	—	—	—	—	—	—	—	—	-6·94	-3·99
20565	-0·97	-2·63	-0·97	-2·07	-1·36	-8·86	-1·17	-10·25	-3·79	-9·70	-5·97	-8·15	-7·21	-1·53

Fig.7/9 $\delta^{13}C$ AND $\delta^{18}O$ COMPOSITION OF DOLOMITES AND POST-DOLOMITE CALCITE

Table of $\delta^{13}C$ and $\delta^{18}O$ values obtained from dolomites and post-dolomite calcites.The zones are identified in the text.

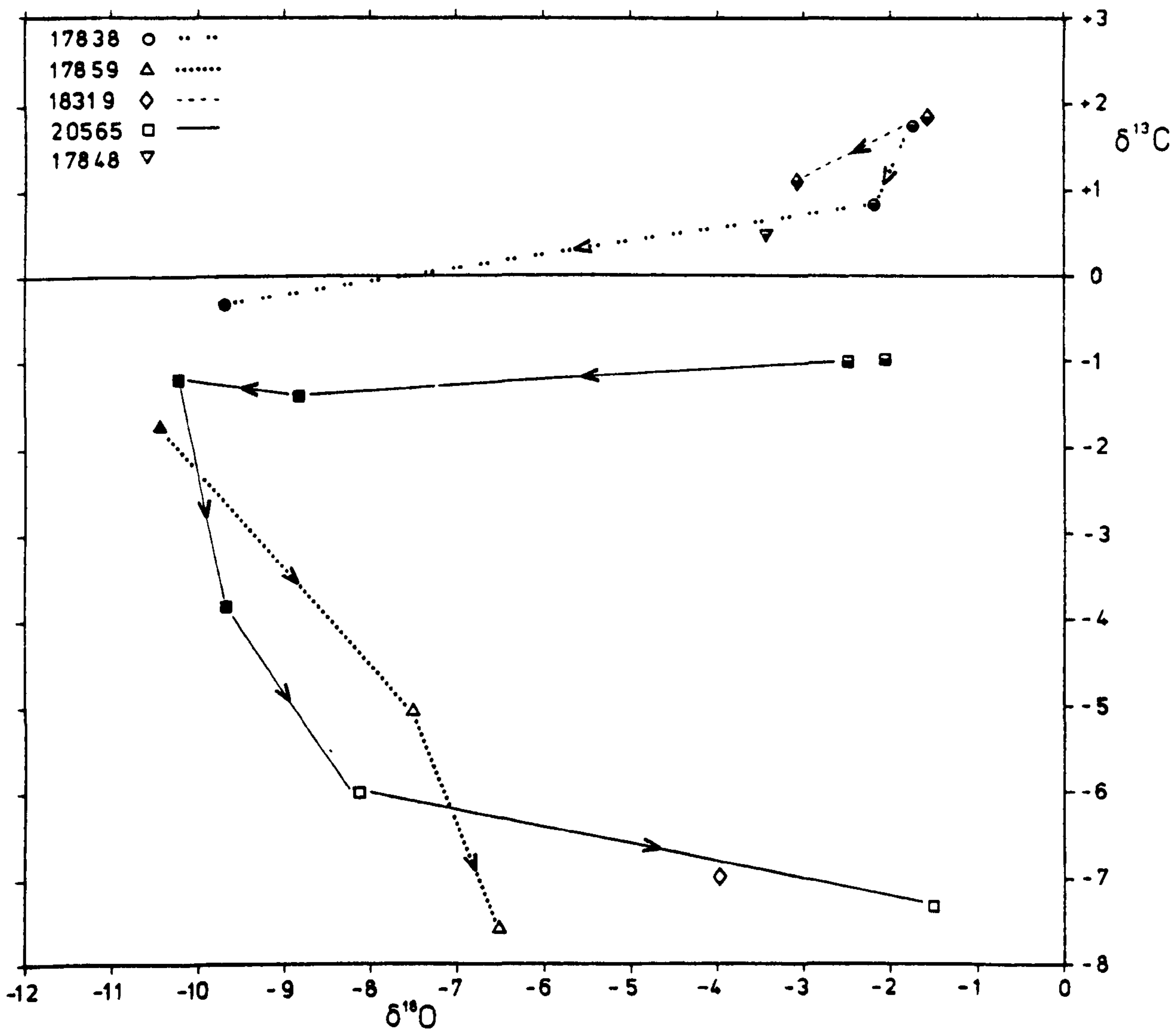


Fig.7/10 $\delta^{13}C$ AND $\delta^{18}O$ COMPOSITION OF DOLOMITES AND POST-DOLOMITE CALCITE

Graph of the $\delta^{13}C$ and $\delta^{18}O$ values obtained from dolomites and post-dolomite calcite. Adjacent samples are connected to show the variation in isotopic composition with time. (open symbols - non-ferroan calcite; solid symbols - ferroan calcite; half filled symbols - dolomite) factor of -3 to -4^{o}/oo, this would mean that the dolomites precipitated from water of a similar isotopic composition as that responsible for the precipitation of the calcite cements. This value for the fractionation factor is not unreasonable bearing in mind the existence of large shelter cavities beneath shells during dolomitisation, which suggests that dolomitisation occurred early in the diagenetic history.

Dolomites that have replaced pre-existing calcite have $\delta^{13}C$ and $\delta^{18}O$ isotopic compositions 1-2^{o}/oo heavier than their sparry counterparts. The replacive dolomites may have inherited some of their isotopic composition from their precursors. This would require the original substrate to have had a near 'normal' marine isotopic composition to account for the shift observed.

Calcite

The first calcite to precipitate after dolomitisation was rich in Fe^{2+} and probably Mn^{2+} (it has very bright CL), with $\delta^{13}C$ = -1.5, $\delta^{18}O$ = -10. These values most closely resemble cements from the Pwll-y-cwm Oolite in the Clydach area although this calcite cannot be correlated with a particular cement zone. Since these calcites are largely restricted to the eastern portion of the outcrop these values do not seem unusual. The change from ferroan to non-ferroan calcite is associated with pyrite precipitation, which is responsible for the removal of Fe^{2+} from the system. Sulphate is needed to accomplish this and must be provided by the influx of new pore fluids. The isotopic composition of these is reflected in the non-ferroan calcites. The most extreme of these calcites has $\delta^{13}C$ = -7.5^{o}/oo, $\delta^{18}O$ = -1.5^{o}/oo. This is by far the heaviest oxygen and lightest carbon found in any of the calcites from the Oolite Group.

There are two obvious sources of sulphate-rich pore fluids:

1. from seawater or from a derivative of seawater
2. from fresh water that has passed through and dissolved evaporites.

If the former were the case the $\delta^{18}O$ values found could reflect either those of 'normal' seawater or seawater that has been enriched in ^{18}O; for example by evaporation. In this case the low $\delta^{13}C$ values could be due to the addition of light carbon from the anaerobic oxidation of organic matter. However, large, sparry calcites are not precipitated from seawater due to the high concentrations of Mg^{2+} (Folk, 1974).

Alternatively, the $\delta^{18}O$ could reflect the precipitation of calcite from low latitude meteoric water, presuming that seawater had a $\delta^{18}O$ with a similar value to that found today. In this case the low carbon values are harder to account for. They are more negative than values found in unaltered allochems and cements that have attributed to a meteoric origin.

It would seem that there is no simple explanation of the source of the fluids responsible for the precipitation of these calcites.

7.5 Concretions

Sample Descriptions

The concretions of the Oolite Group are described in Chapter 5. Samples were scraped from stained slabs.

Results

The results of analyses are presented in Figs. 7/11 and 12. The isotopic composition of the concretions is very similar to that of the cements. Different types of concretions fall in different fields.

Fig.7/11 $\delta^{13}C$ AND $\delta^{18}O$ COMPOSITION OF CONCRETIONS

Table of $\delta^{13}C$ and $\delta^{18}O$ values obtained from concretions. Arrows indicate progressive samples through a specimen.

CONCRETION TYPE	POSITION	SAMPLE NO.	inclusion poor columnar calcite		inclusion rich columnar calcite		recrystallized microspar		acicular calcite		white calcite		ferroan dolomite		Fe calcite filled vugs		microspar		veins (ferroan - ■)		COMMENTS
			$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	
CALCRETE	GILWERN OOLITE	17843	–	–	–	–	–	–	–	–	–	–	–	–	–	–	-4.55	-5.88	–	–	fine grained
																	-5.11	-6.71			coarse "
		17858	–	–	–	–	–	–	–	–	–	–	–	–	–	–	-5.37	-6.21	–	–	coarse "
		18310	–	–	–	–	–	–	–	–	–	–	–	–	–	–	-5.24	-6.29	–	–	fine "
																	-4.77	-6.35			coarse " ; mildly ferroan
(crusts)	CLYDACH BEDS	20575	–	–	–	–	–	–	–	–	–	–	–	–	–	–	-4.07	-6.87	–	–	
		20576	–	–	–	–	–	–	–	–	–	–	–	–	–	–	-3.55	-7.71	–	–	
	BLAEN ONNEU OOLITE	20542	–	–	–	–	–	–	–	–	–	–	–	–	–	–	-4.07	-7.41	–	–	
RECRYSTALLIZED CALCRETE	BLAEN ONNEU OOLITE	17889	–	–			-5.34	-8.32	–	–	–	–	–	–	-3.88	-9.65	–	–	–	–	
							-4.17	-8.34													
					-5.94	-8.49															
		22352	–	–	-5.51	-8.27			–	–	–	–	–	–	–	–	–	–	–	–	
							-5.82	-8.29													
					-6.49	-8.09															
		22353	–	–	-3.46	-7.46			–	–	–	–	–	–	-3.73	-8.79	–	–	–	–	
							-4.62	-7.83													
BOTRYOIDAL	DAREN DDÛ BEDS	17907	–	–	–	–	–	–	-3.54	-8.11	-3.09	-7.71	–	–	–	–	–	–	-3.07	-7.97	
									-3.95	-8.83	-3.11	-7.90									
		17910	–	–	–	–	–	–	-3.17	-8.40	-3.99	-8.40	-2.52	-3.21	–	–	–	–	–	–	
									-3.79	-7.75	-4.11	-7.51									
											-4.18	-7.95									
MASSIVE / COLUMNAR	DAREN DDÛ BEDS	17895	–	–	–	–	-5.44	-7.85	–	–	-5.50	-7.17	–	–	-4.11	-10.13	–	–	-3.26	-7.21	● from black 'nucleus'
											-5.39	-7.11									
											5.37	7.08									
		18144	-4.40	-7.89			-5.05	-8.26	–	–	-5.16	-7.93	–	–	-4.22	-10.26	–	–	5.31	7.31	▲ progressive samples from longitudinal section
					-4.59	-7.68															
			-3.47	-7.47																	⬮ from above geopetal internal sediment
					-3.79	-7.39															
			-5.47	-7.44																	
			-5.01	-7.79																	
		18145	-5.43	-7.56	-5.34	-7.61	–	–	–	–	–	–	–	–	–	–	–	–	–	–	◆ from transverse section
					-4.90	-7.70															◇ ferroan outer margin
		22354	–	–	–	–	-4.90	-7.75	–	–	-5.71	-7.65	–	–	-4.25	-10.51	–	–	-5.27	-7.52	
(fibrous sheets)	CLYDACH BEDS	20554	–	–	-4.08	-7.37	–	–	–	–	–	–	–	–	–	–	–	–	–	–	
					-4.50	-7.52															o etched and filled by ferroan calcite
		20576	–	–	-2.39	-7.37	–	–	–	–	–	–	–	–	–	–	–	–	–	–	

Fig.7/12 $\delta^{13}C$ AND $\delta^{18}O$ COMPOSITION OF CONCRETIONS

Graphs of the $\delta^{13}C$ and $\delta^{18}O$ values obtained from concretions.

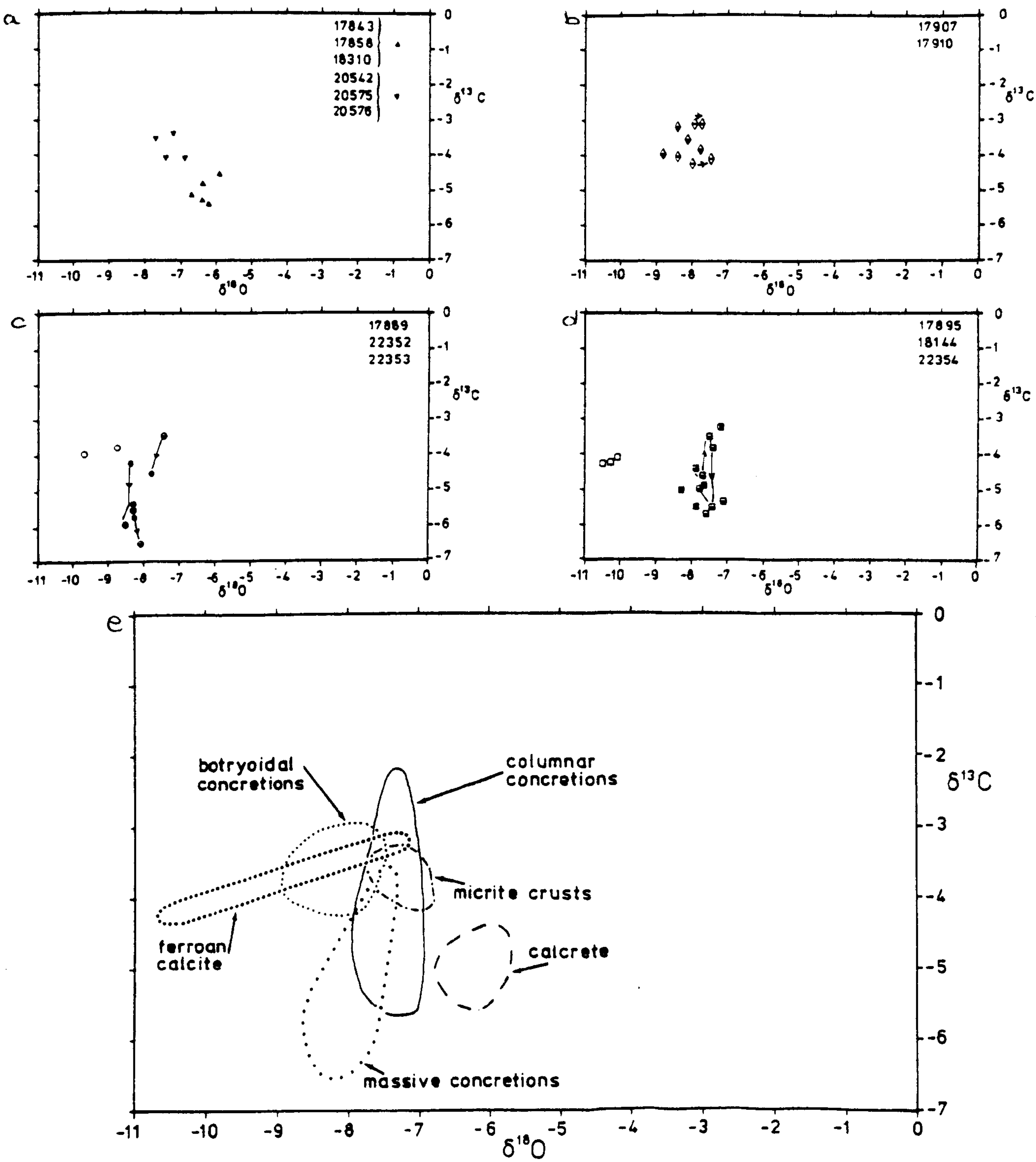
a) From calcrete(triangle, apex up) and micrite crusts(triangle, apex down).

b) From botryoidal concretions(open diamonds) and associated calcite spar(half filled diamonds).

c) From recrystallised calcrete concretions(solid circle - microspar; open circle - ferroan calcite; half filled circle - fibrous calcite).

d) From massive(solid square)/columnar(half filled square) concretions.(open square - ferroan calcite; open square with vertical line - non-ferroan calcite)

e) Graph showing the fields into which the values obtained from specific concretion types fall.



a
17843
17858
18310
20542
20575
20576
b
17907
17910
c
17889
22352
22353
d
17895
18144
22354
e
botryoidal concretions
columnar concretions
micrite crusts
ferroan calcite
calcrete
massive concretions
δ13C
δ18O

Discussion

Concretions associated with exposure

The calcrete from the top of the Gilwern Oolite should give a direct indication of the isotopic composition of meteoric waters at the time when the top of the Gilwern Oolite was exposed. The preservation of sharp chemical zonation suggests that there has been no recrystallisation and possibly no alteration of the original isotopic composition. The calcrete has similar isotopic composition as cements from the very top of the Gilwern Oolite (Fig. 7/12a), although these tend to have lighter carbon ratios than the calcrete. The interpretation of these values has already been discussed.

Calcrete from the top of the Gilwern Oolite is isotopically distinct from other soil profiles from within the Oolite Group (Fig. 7/12a, b, e), these having oxygen values 1-2^{o}/oo lighter and a much wider spread of carbon values. Recrystallised calcrete nodules from the top of the Blaen Onneu Oolite show a decrease in $\delta^{13}C$ outwards that is irrespective of the fabric. Micrite crusts fall at the top of the trend shown by these samples. Their values are probably not original but attained when they recrystallised.

Massive/columnar concretions

These concretions from the Daren Odu Beds have similar isotopic values to the recrystallised calcretes. No progressive change is found along the columnar calcite crystals (Fig. 7/12d), although a wide range of $\delta^{13}C$ values may exist within a single crystal. Marshall (1982) also observed a wide range of isotopic values within columnar calcites from several localities. Ferroan calcites fall in a linear trend that is distinct from the rest of the concretion and which is coincident with the trend found in

Zone 6 cements. Therefore, it is thought that these ferroan calcites are coeval with Zone 6 cements. The distinction between ferroan calcites and the rest of the concretion indicates that the concretion gained its present isotopic composition prior to Zone 6 precipitation. These values are unlikely to be original as the concretions are recrystallised.

$\delta^{18}O$ values are very similar to those found by Marshall (1982), but they display a much narrower range. The similarity in the $\delta^{18}O$ values between these concretions and the cements of the Oolite Group suggest that they formed from similar pore waters as the cements during burial. Marshall (1982) discusses possible mechanisms for the reversal of isotopic trends. Of his suggestions the most likely to apply to these concretions is that of an external supply of pore waters - it is known that pore water chemistry changed many times during diagenesis. $\delta^{13}C$ values are very similar to those found in cements and are thought to have a similar origin.

Botryoidal concretions

These concretions fall in a group distinct from the other concretions, having a more negative oxygen value (Fig. 7/12e). This may have resulted from recrystallisation at slightly greater depth and temperature than the other Daren Ddu Bed concretions. Their carbon values lie at the top of the range exhibited by other concretions. The sparry calcites that fill fractures have similar values as the fibrous calcite. This is slightly heavier than Zone 4 cement. Baroque dolomite is similar to that found elsewhere in the Oolite Group. Ferroan calcite falls on the Zone 6 trend.

Interpretation of the isotopic composition of the concretions is difficult. The values found today are unlikely to be original.

The similarity of the isotopic values with Zone 4 cement suggests that recrystallisation occurred in water similar to that which precipitated these cements. It must have occurred prior to Zone 6 precipitation. The relationship between sparry calcite found within certain concretions and calcite cements is unclear, but there is good correlation between ferroan calcite and baroque dolomite found within concretion and Zones 6 and 7 cement.

7.6 Conclusions

1. The composition of Carboniferous seawater

There is no decisive evidence as to the isotopic composition of Carboniferous seawater. The re-equilibration trend of allochems suggests that the ^{13}C was much as it is today. The same trend points to a $\delta^{18}O$ of up to 6 to 7^{o}/oo lighter than found today. The uncertainty in knowing the exact composition of meteoric water means that no exact figure can be put on the depletion of ^{18}O. No additional evidence is provided by the cements or concretions. The post-dolomite calcites, with a $\delta^{18}O = -1.5^{o}$/oo, have the heaviest oxygen values found within the Oolite Group and these may reflect seawater values. If this is the case this value falls well within the ranges suggested by Brand & Veizer (1981) and Brand (1982) for the oxygen isotopic composition of Carboniferous seawater.

2. Origin of the variations in the isotopic composition found

That such a wide variation in isotopic values is found in the Oolite Group demonstrates that re-equilibration has only been of minor importance. Various processes explain the variations that are found.

a. Re-equilibration - this caused the variation seen in the values of the allochems and Zone 2a cements. It occurred 'early' in the diagenetic history and no other re-equilibration events have influenced the Oolite Group subsequently.

b. Variations in pore fluid isotopic composition - this caused the variations seen in the cements and post-dolomite calcites. These changes are not the result of temperature effects.

c. Variations in fractionation factors with temperature - this has resulted in the very light $\delta^{18}O$ values found in some veins.

d. Variations in fractionation factors between minerals - this has obviously played some part in the variation between calcite and dolomite isotopic compositions. The extent of this effect is unclear due to the uncertainty in the value of the fractionation factor.

3. <u>The composition of meteoric water</u>

Evidence from calcrete and the re-equilibration trend of marine allochems suggests that meteoric water had an isotopic composition with $\delta^{18}O = -6.5$, $\delta^{13}C = -5^{o}/oo$. The reason for the light ^{18}O value is at least in part due to lighter seawater in Carboniferous seas. Light ^{13}C reflects the addition of light soil gas CO_2.

4. <u>Dolomitisation</u>

The fluids responsible for dolomitisation in the east of the outcrop had normal marine $\delta^{13}C$. The $\delta^{18}O$ was possibly similar to that of the fluids precipitating carbonate cements. This will depend on the fractionation factor between calcite and dolomite.

CHAPTER EIGHT

DISCUSSION AND CONCLUSIONS

8.1 Diagenetic history

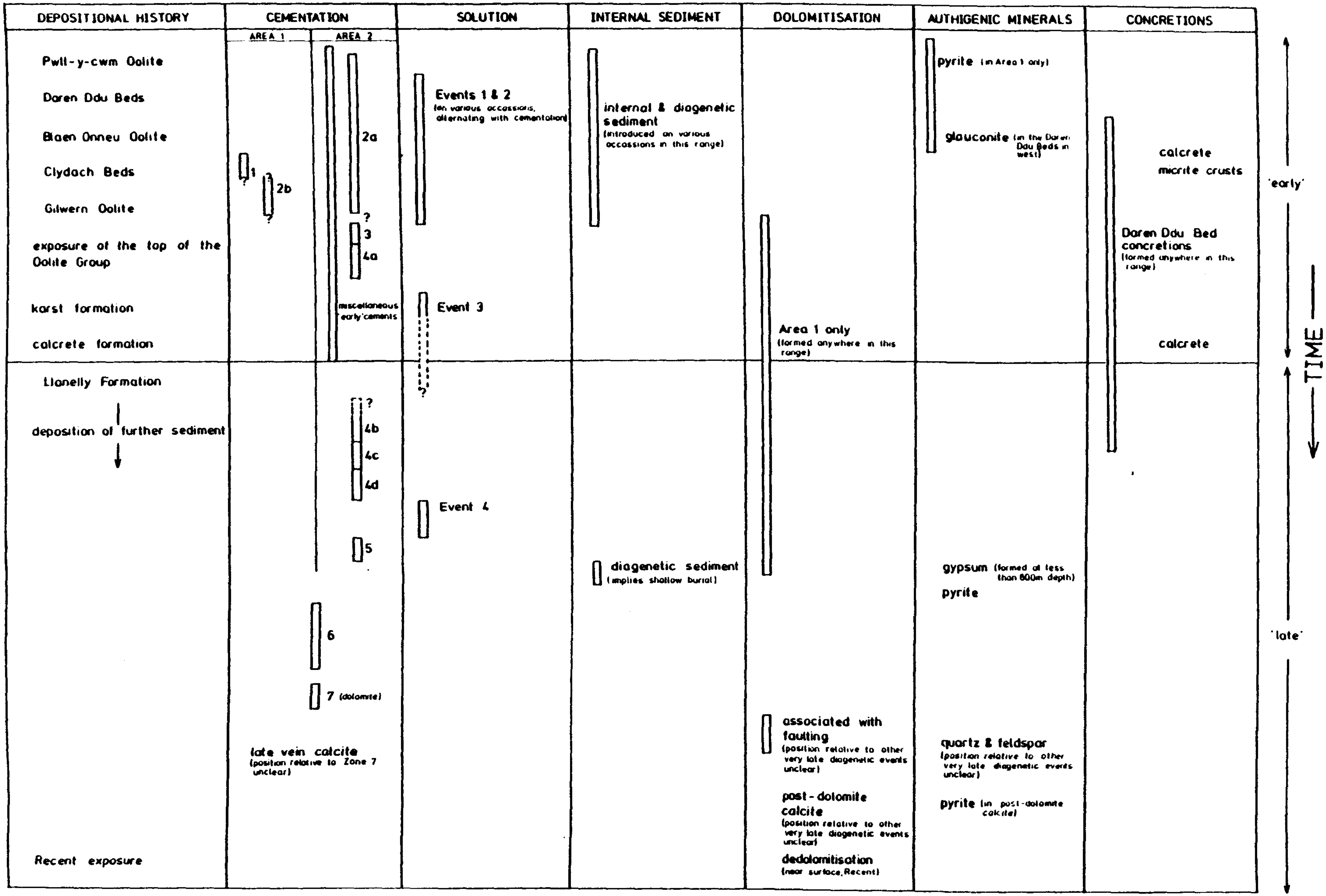
In Chapters 2 to 6 the major diagenetic events that affected the Oolite Group were described and discussed. These are not the only events that occurred, but other events are only of minor importance e.g. grain to grain pressure solution, stylolitisation, fracturing. The major diagenetic events are summarised in Fig. 8/1. Although the relative timing of most of the diagenetic events, except the very latest ones, is clear, the duration of each event is usually uncertain. Hence it is usually impossible to put an absolute age on the events.

The relative timing of diagenetic events post-dating the precipitation of Zone 6 cement is unclear. This is largely because the products of later events are isolated from each other and so their inter-relationship cannot be judged. Very late calcite is restricted to veins and a more detailed investigation of the cross-cutting nature of these could party resolve this problem.

There are some clues that can be used as guidelines to indicate the absolute ages of diagenetic events. The presence of pseudomorphs of gupsum associated with diagenetic sediment suggests that all events preceeding these occurred at less than 800 m.burial, the approximate depth at which gypsum dehydrates to anhydrite (Berner, 1971). By considering the probable thickness of over-

Fig.8/1 DIAGENETIC EVENTS AFFECTING THE OOLITE GROUP

The major diagenetic events affecting the Oolite Group are summarised.The timing of events relative to sedimentation is shown.Except for some 'early' events the absolute timing of events is unknown.In very 'late' diagenesis even the relative timing of events is unknown.The relative period in which an event occurred is indicated by a column.An event did not necessarily last the duration indicated by the column,which merely indicates its position in relation to sedimentation and other diagenetic events.Where the period over which an event occurred is unclear this is indicated by a dotted column.


DEPOSITIONAL HISTORY
CEMENTATION
SOLUTION
INTERNAL SEDIMENT
DOLOMITISATION
AUTHIGENIC MINERALS
CONCRETIONS
AREA 1
AREA 2
Pwll-y-cwm Oolite
Daren Ddu Beds
Blaen Onneu Oolite
Clydach Beds
Gilwern Oolite
exposure of the top of the Oolite Group
karst formation
calcrete formation
Llanelly Formation
deposition of further sediment
Recent exposure
1
2a
2b
3
4a
miscellaneous 'early' cements
4b
4c
4d
5
6
7 (dolomite)
late vein calcite
(position relative to Zone 7 unclear)
Events 1 & 2
(on various occassions, alternating with cementation)
Event 3
Event 4
internal & diagenetic sediment
(introduced on various occassions in this range)
diagenetic sediment
(implies shallow burial)
Area 1 only
(formed anywhere in this range)
associated with faulting
(position relative to other very late diagenetic events unclear)
post-dolomite calcite
(position relative to other very late diagenetic events unclear)
dedolomitisation
(near surface, Recent)
pyrite (in Area 1 only)
glauconite (in the Daren Ddu Beds in west)
gypsum (formed at less than 800m depth)
pyrite
quartz & feldspar
(position relative to other very late diagenetic events unclear)
pyrite (in post-dolomite calcite)
calcrete
micrite crusts
Daren Ddu Bed concretions
(formed anywhere in this range)
calcrete
'early'
'late'
TIME

lying sediments, now eroded, this suggests that all diagenetic events preceeding and including gypsum precipitation occurred during the latter stages of the deposition of the Millstone Grit, i.e. all events preceeding gypsum precipitation are at the latest mid-Carboniferous in age.

The diagenetic events that affected the Oolite Group reflect the many changes in the nature of the pore waters that infiltrated the Group. This resulted in alternating periods of solution and cementation and later in the precipitation of sulphate minerals. Later in this chapter the nature and origin of the pore waters that passed through the Oolite Group will be considered and paleohydrological models will be developed.

8.2 The origin of the pore waters affecting the Oolite Group

The chemistry of pore waters can be partly deduced from the diagenetic affects, if any, that they produce. Cements are particularly important in this respect.

The chemistry of cements as deduced from staining and CL

From staining:

The presence of Fe^{2+} in the calcite lattice can be detected by staining with potassium ferricyanide (Freidman, 1959; Dickson, 1966; Evamy, 1963). This is usually used in association with Alizarine red-S. Lindholm & Finkelman (1972) used staining as a semi-quantitative method of determining the amount of Fe^{2+} in calcite. Many variables affect the colour and intensity of the stain so this is an unreliable method. Lindholm & Finkelman (1972) separated three classes of ferroan calcite:

Class I 2,900 to 8,700 ppm, staining red/purple

Class II 8,700 to 14,500 ppm, staining purple

Class III 14,500 to 20,300 ppm, staining purple/blue.

It would appear that the detection limit of the method is approx. 2,900 ppm. Oldershaw & Scoffin (1967) report being able to detect 200 ppm Fe^{2+} by staining. Zones 3 and 5 of this study fall into Class I, perhaps II. Zone 6 falls into Class III. These values should not be taken too seriously, but they are the only guidelines available.

From CL:

Mn^{2+} is regarded as an 'activator' producing luminescence, whereas Fe^{2+} is regarded as a 'quencher' inhibiting luminescence. Sommer (1972) suggests that Mg^{2+} also may act as a quencher, but Harwood (pers. comm.) thinks that it may be an activator in ~~dolomite~~ calcite. Other than Mg^{2+} all cations thought to affect luminescence in carbonates, e.g. Co^{2+} and Ni^{2+}, which are thought to act as 'quenchers', are present in very low concentrations compared to Mn^{2+} and Fe^{2+} and so these two cations are widely thought to be the dominant controls on luminescence (Sommer, 1972; Oglesby, 1976; Meyers, 1974, 1978; Nickel, 1978; Pierson, 1981; Frank et al, 1982).

Mn^{2+} and Fe^{2+} act in opposing directions, the former causing, the latter inhibiting, luminescence. The nature of the interaction of these two cations is not fully understood. Ferroan calcites can luminesce very brightly. Indeed, some of the most brightly luminescing calcites found in the Oolite Group are highly ferroan. Pierson (1981) suggests that below concentrations of 10,000 ppm (1 wt%), Fe^{2+} has little influence on CL, but above this value CL is rapidly quenched. Others consider the ratio of Fe^{2+}/Mn^{2+} to be the controlling factor (Fairchild, 1978; Frank et al, 1982). Martin & Zeeghers (1969) and Meyers (1974) suggest that 1000 ppm Mn^{2+} to be the minimum required to cause CL. However, Pierson (1981) has found that as little as 100 ppm Mn^{2+} can produce CL in dolomite.

Bearing in mind the above discussion it can be seen that few conclusions can be drawn about the chemistry of cements from their CL. It will be assumed below that Mn^{2+} is the cause of CL in the calcites of the Oolite Group. No conclusions can be drawn about the concentration of Mn^{2+} present in the luminescing zones.

The significance of isotope and trace element chemistry in determining the origin of pore fluids

Variations in Fe^{2+} and Mn^{2+} in calcite can be the result of a number of causes:

1. variations in the concentration of these ions in the pore water in constant, reducing conditions;
2. variations in Eh in the presence of sufficient Fe^{2+} and Mn^{2+}, the zones free of these trace elements representing oxidising conditions and the zones rich in these trace elements representing reducing conditions;
3. variations in the SO_4^{2-} content of the pore waters in reducing conditions, when SO_4^{2-} is abundant in reducing conditions Fe^{2+} and Mn^{2+} will be removed in sulphide minerals rather than entering the calcite lattice (Evamy, 1969).

Any one or combination of these factors can act at a given time. Most of the cements of the Oolite Group were precipitated at shallow depths and at least the Mn^{2+} distribution co-efficient is not sensitive to changes in temperature (Bodine et al, 1965). Hence it is thought that temperature and perhaps pressure are not important factors. Recent shallow carbonate terrains have a fairly constant pore water pH (Back & Hanshaw, 1970; Hem, 1970). Since pore water chemistry is known to have changed many times in the Oolite Group it cannot be assumed that pH was constant. Therefore pH may have been an important factor, although it is thought unlikely. The factors listed in 1-3 above will largely control the CL of calcites.

Oglesby (1976) has devised a model to predict the CL properties of calcites in different Eh/pH conditions. He also mentions the importance of other factors such as pCO_2.

A knowledge of the Mg^{2+} content of the calcite is important in deducing the nature of the pore waters from which they are precipitated. Mg^{2+} is low in meteoric waters and one would expect calcites precipitated from this type of pore water to have a low Mg^{2+} content (<0.3 mole% $MgCO_3$). Mixing with marine pore waters increases the Mg^{2+} content and calcites precipitated from pore waters with a marine component would have a higher Mg^{2+} content (>0.8 mole% $MgCO_3$). Unfortunately, it is not possible to deduce the Mg^{2+} content of the calcites of the Oolite Group from the available data. The presence or absence of Mg^{2+} in calcite greatly affects the form in which it is precipitated (Folk, 1971; Berner, 1972). The equant, blocky nature of most of the calcites in the Oolite Group suggests low Mg^{2+} contents.

Oxygen and carbon isotope results indicate a strong meteoric influence. Only cements from the Pwll-y-cwm and Blaen Onneu Oolites in the Clydach area show any sign of a marine influence: zero or slightly positive $\delta^{13}C$ values. These are thought to result by re-equilibration of meteoric water with allochems that have marine $\delta^{13}C$ compositions, so are not a reflection of the original pore water. Allochems and Zone 2a cements are thought to have secondary meteoric-like isotope values; due to re-equilibration with meteoric waters.

The dolomites of Zone 7 must have been precipitated from pore waters with high Mg/Ca ratio. These occur late in diagenesis and are likely to have formed at greater depths than the calcite cements. The origin of the pore waters from which they are precipitated is unknown. Isotope data is inconclusive on this point.

The CL of Zone 4 (of this study) is very similar to Zones 1 and 3 of Meyers (1978), which he interpreted as products of a shallow meteoric groundwater system which was oxidising and/or deficient in Fe^{2+} and Mn^{2+}. A similar interpretation seems likely for Zone 4 of this study. Zone 4a was interpreted as being associated with exposure at the top of the Oolite Group purely on petrographic grounds. Within Zone 4 the brightly luminescing hairline subzones tend to occur in clusters. This is thought to reflect fluctuations in Eh about the level at which Mn^{2+} starts to be incorporated into calcite (Eh = 0.6, Ogelsby, 1976). Slight Eh fluctuations at this level would cause the alternate inclusion and exclusion of Mn^{2+} in the calcite lattice. In areas of Zone 4 where no hairline subzones are present, conditions are thought to have been more oxidising and small fluctuations in Eh were not sufficient to result in Mn^{2+} being incorporated into calcite. This presumes that there is always sufficient Mn^{2+} in solution to cause CL if incorporated.

The information available about cement Zones 1-7 is summarised in Fig. 8/2.

8.3 Paleohydrology

The significance of the identification of discrete cement zones and solution events

The presence of discrete cement zones and solution surfaces in the cements of the Oolite Group illustrates that during diagenesis a large number (more than 6) of chemically distinctive pore waters have passed through the rocks of the Oolite Group. These have varied in their chemistry, degree of $CaCO_3$ saturation and Eh. There were periods when pore waters were saturated with respect to calcite,

	DATA				DEDUCED ENVIROMENT				
ZONE	Fe^{2+}	Mn^{2+}	$\delta^{13}C$	$\delta^{18}O$	SO_4^{2-}	Mg^{2+}	Eh	ORIGIN	COMMENTS
1	III	?	marine	?	none	?	reducing	?	
2a	none	none	meteoric	meteoric	?	?	?	marine ?	isotopes reequilibrated with meteoric water, lack of Mn^{2+} and Fe^{2+} may reflect strongly oxidising conditions or the lack of these ions in the pore waters
2b	none	present	marine	?	?	?	slightly oxidising	?	
3	I(II?)	present	meteoric	meteoric	none	?	reducing	meteoric	
4	none	present only in hairline zones	meteoric	meteoric	?	?	oxidising, at least where Mn^{2+} present	meteoric	lack of Mn^{2+} and Fe^{2+} may reflect strongly oxidising conditions or the lack of these ions in the pore water
5	I	present	meteoric	meteoric	none	?	reducing	meteoric	
6	III ⟶ none with time	?	meteoric / marine	meteoric	none	?	reducing, at least while ferroan	meteoric ?	isotope values fall on a straight line, which suggests mixing of pore waters
7	present	?	?	?	none	high	reducing	?	dolomite

Fig.3/2 INFORMATION DEDUCED ABOUT THE CHEMISTRY OF THE CEMENT ZONES

Table summarising chemical data for the cement zones and their precipitation enviroments deduced from this. The amount of Fe^{2+} present is given in terms of the ferroan calcite classes of Lindholm & Finkelman (1972). A question mark indicates where no firm conclusion can be drawn.

and cement was precipitated, and there were periods when the pore waters were undersaturated, and cements were dissolved. Since cement zones and solution events can be correlated over a wide area, Pwll du to Cwar y Ystrad, this involves the movement of large volumes of chemically distinct pore waters. Such changes can be achieved in a number of ways:

1. changes in sea-level can shift the position of the freshwater, phreatic lens, to which cementation is largely restricted (Meyers, 1978). This may be in response to local tectonic affects or worldwide changes in sea-level;
2. changes in chemistry of the pore waters of the phreatic lens perhaps in response to changes in influx in the catchment area (Steinen et al, 1978);
3. spatial changes in the phreatic lens perhaps associated with changes in influx in the catchment area (Steinen et al, 1978).

Such changes are likely to have affected the Oolite Group. Exposure surfaces, karsts and calcretes, alternate with marine sediments both in the Oolite Group and in the overlying limestone. This would result in a changing position of the freshwater phreatic lens. This, in part, may be in response to tectonic events (Owen, 1971) as well as eustatic changes in sea level (Ramsbottom, 1973).

'Early' diagenesis

In the study area there is abundant evidence of exposure during sedimentation, the more so as one moves northwestwards, i.e. shorewards. At various times during the sedimentation of the Oolite Group, in the study area, marine pore waters would have been replaced, at least in part, by freshwater. The Ghyben-Hertzberg principle (Ward, 1967, p. 287) states that for every metre of freshwater that lies above mean sea-level, the thickness of the freshwater lens floating on salt water of ocean density is about 40 metres. When exposed, the Oolite Group lay very near the coast so that the freshwater would not lie much above sea-level. However, if the water table lay only ¼ m. above mean sea-level, the freshwater lens would extend down 10 m. below sea-level. Exposure during the initial stages of sedimentation of the Oolite Group would have resulted in all marine pore waters being expelled from the Oolite Group. During later sedimentation exposure may have resulted in marine porewaters being expelled only from the top of the Oolite Group. The phreatic lens would have to stand at least 1 m above mean sea-level to expel all marine pore water from the whole thickness of the Oolite Group. 'Early' sparry calcites were precipitated in such thin pheatic zones.

The most abundant 'early' cements are associated with the top of the Oolite Group. A model of the paleohydrology associated with their formation is presented in Fig. 8/3. Zone 3 cements can be divided into those that are ferroan and those that are not. This is thought to be the result of a change from oxidising to reducing conditions with increasing depth (Fig. 8/3-1). Zone 4a cements were precipitated below the water table at the top of the Oolite Group (Fig. 8/3-2). Erosion and karst formation resulted in the distribution of these cement zones seen today (Fig. 8/3-3). The Zone 3 cements are only of a non-ferroan nature at the southeastern end of the outcrop. The junction between ferroan and non-ferroan Zone 3 occurs at progressively higher levels the further northwestwards one looks. At the northwestern end of the study area only ferroan Zone 3 is found, non-ferroan Zone 3 having been removed by erosion. Likewise Zone 4a has also been removed from the northwestern end of the outcrop. Solution of Zones 3 and 4a cements resulted from the

Fig.8/3 PALEOHYDROLOGY ASSOCIATED WITH THE FORMATION OF CEMENT ZONES 3 AND 4a

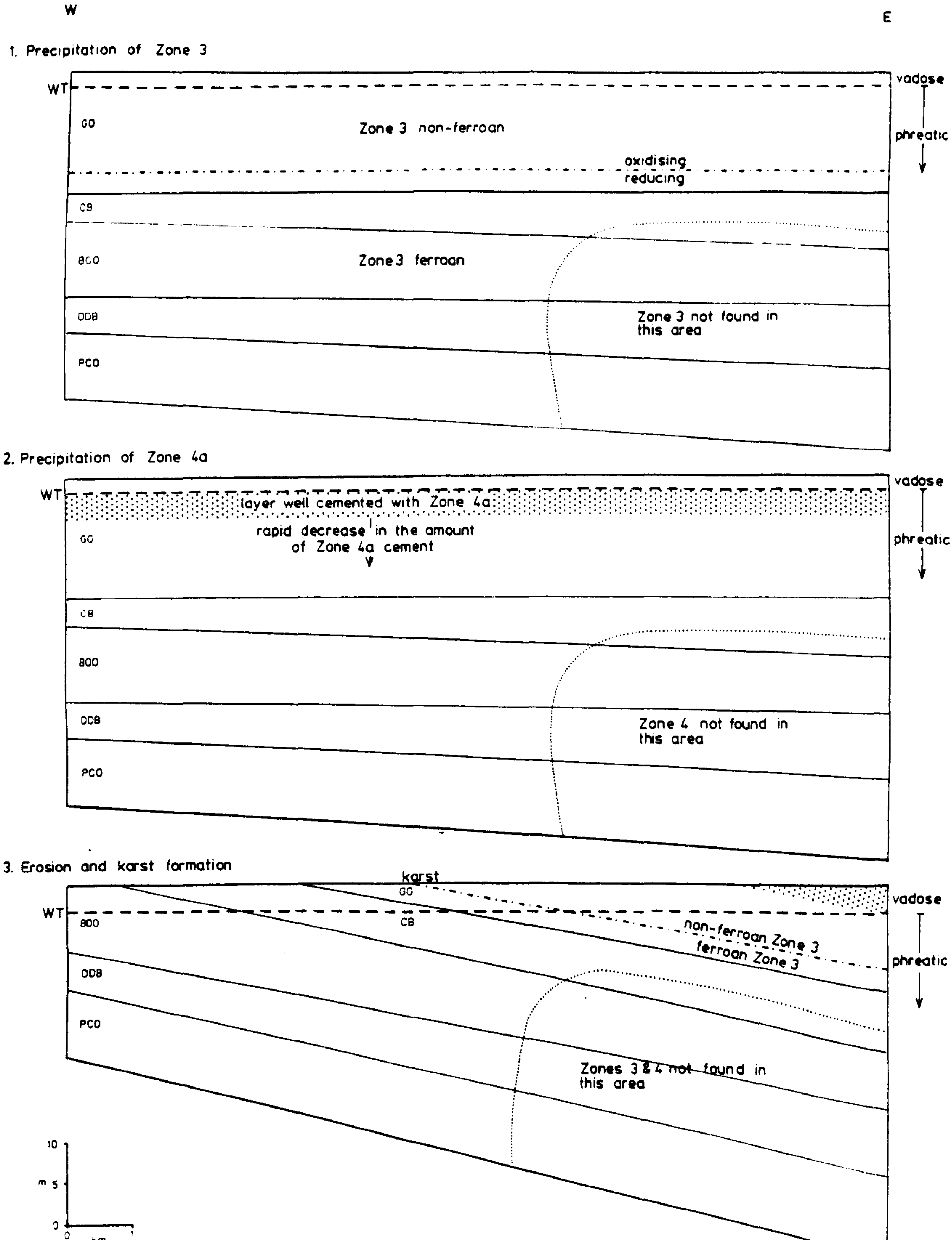
Three diagrams tracing the development of Zone 3 and 4a cements.

1) Zone 3 is precipitated below the water table(WT). Near the base of the Gilwern Oolite there is a change from oxidising to reducing conditions resulting in Zone 3 being ferroan in the lower part of the Oolite Group.

2) Much Zone 4a cement is precipitated near the top of the Gilwern Oolite, just below the water table(WT). There is a rapid decrease in the amount of cement precipitated downwards.

3) Erosion and karst formation removes the top of the Oolite Group. Progressively more is removed the further west one looks. This results in the distribution of Zone 3 and 4a cements seen today.

During the time period considered above Zone 3 and 4a cements were not precipitated in Diagenetic Area 1. This area is outlined by a fine, stippled line.


W
E
1. Precipitation of Zone 3
WT
vadose
phreatic
GO
Zone 3 non-ferroan
oxidising
reducing
CB
BOO
Zone 3 ferroan
DDB
Zone 3 not found in this area
PCO
2. Precipitation of Zone 4a
WT
vadose
layer well cemented with Zone 4a
phreatic
GO
rapid decrease in the amount of Zone 4a cement
CB
BOO
DDB
Zone 4 not found in this area
PCO
3. Erosion and karst formation
karst
GO
vadose
WT
BOO
CB
non-ferroan Zone 3
ferroan Zone 3
phreatic
DDB
PCO
Zones 3 & 4 not found in this area
10
m 5
0
0
km
1

influx of undersaturated pore waters during karst formation at the top of the Oolite Group. Fig. 8/4 shows in more detail the development of the top of the Oolite Group in the southeastern end of the outcrop. Zone 4a was precipitated near the top of the Oolite Group in the phreatic zone. The rapid decrease in the amount of this cement downwards has been considered already (Fig. 8/4-1). The erosion associated with karst formation resulted in a lowering of the land surface and watertable. Hence, the watertable came to lie in rocks that had formerly been cemented in the phreatic zone (Fig. 8/4-2). Further erosion resulted in the land surface truncating the phreatically cemented rocks, and the watertable lay below the level of the phreatically cemented layer. Meniscus cements were precipitated between the watertable and the base of the phreatically cemented layer (Fig. 8/4-3). This was followed by calcrete formation (Fig. 8/4-4). It is clear from the isotope data that during exposure of the top of the Oolite Group the meteoric ground water system extended at least 30 m below the surface (Fig. 7/3). Earlier meteoric ground water systems seem not to have had a significant affect on the isotopes of the allochems, perhaps due to their limited extent and residence time within the Oolite Group. The difference in CL between Zones 3 and 4a must reflect a difference in the chemistry of the pore fluids from which they were precipitated. It has already been stated that Zone 4a is of shallow meteoric origin. The difference between this and Zone 3 may be due to them being precipitated from different portions of the phreatic lens, but this is only speculation and there is no evidence to use as a guide in the interpretation of this difference.

Fig.8/4 THE DEVELOPMENT OF THE KARST AT THE TOP OF THE GILWERN OOLITE

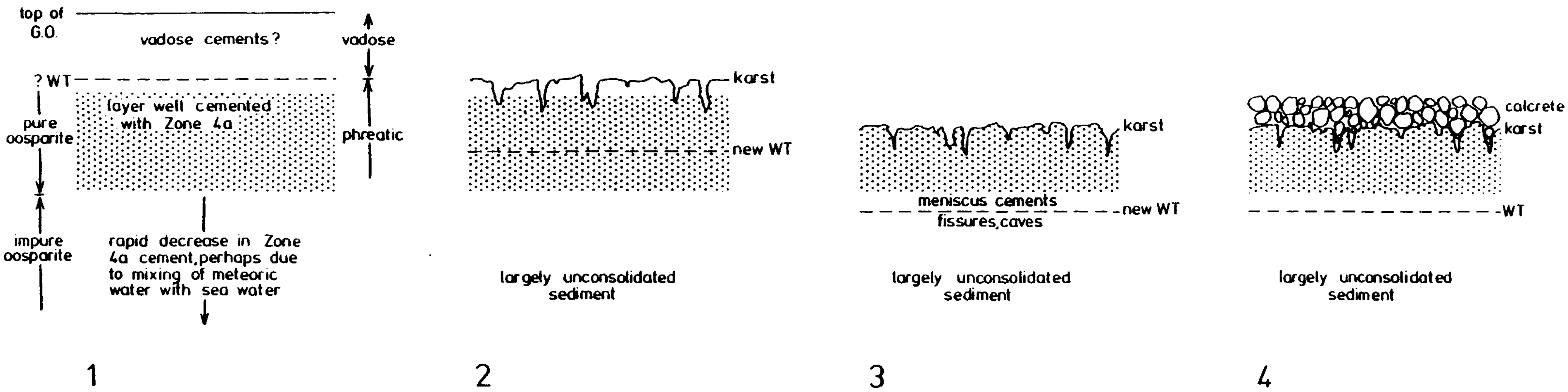
Four diagrams trace the development of the karst at the top of the Gilwern Oolite.

1)A well cemented layer develops just below the water table(WT).

2)Solution of the exposed surface results in the development of a karst.

3)Continued erosion results in a drop in the water table(WT) below the well cemented layer so that phreatically cemented rock lays in the vadose zone. Meniscus cements are precipitated between the well cemented layer and the new water table(WT).

4)Karst development is replaced by calcrete formation.


top of
G.O.
vadose cements?
vadose
? WT
layer well cemented
with Zone 4a
pure
oosparite
phreatic
impure
oosparite
rapid decrease in Zone
4a cement, perhaps due
to mixing of meteoric
water with sea water
1
karst
new WT
largely unconsolidated
sediment
2
karst
meniscus cements
new WT
fissures, caves
largely unconsolidated
sediment
3
calcrete
karst
WT
largely unconsolidated
sediment
4

'Late' diagenesis

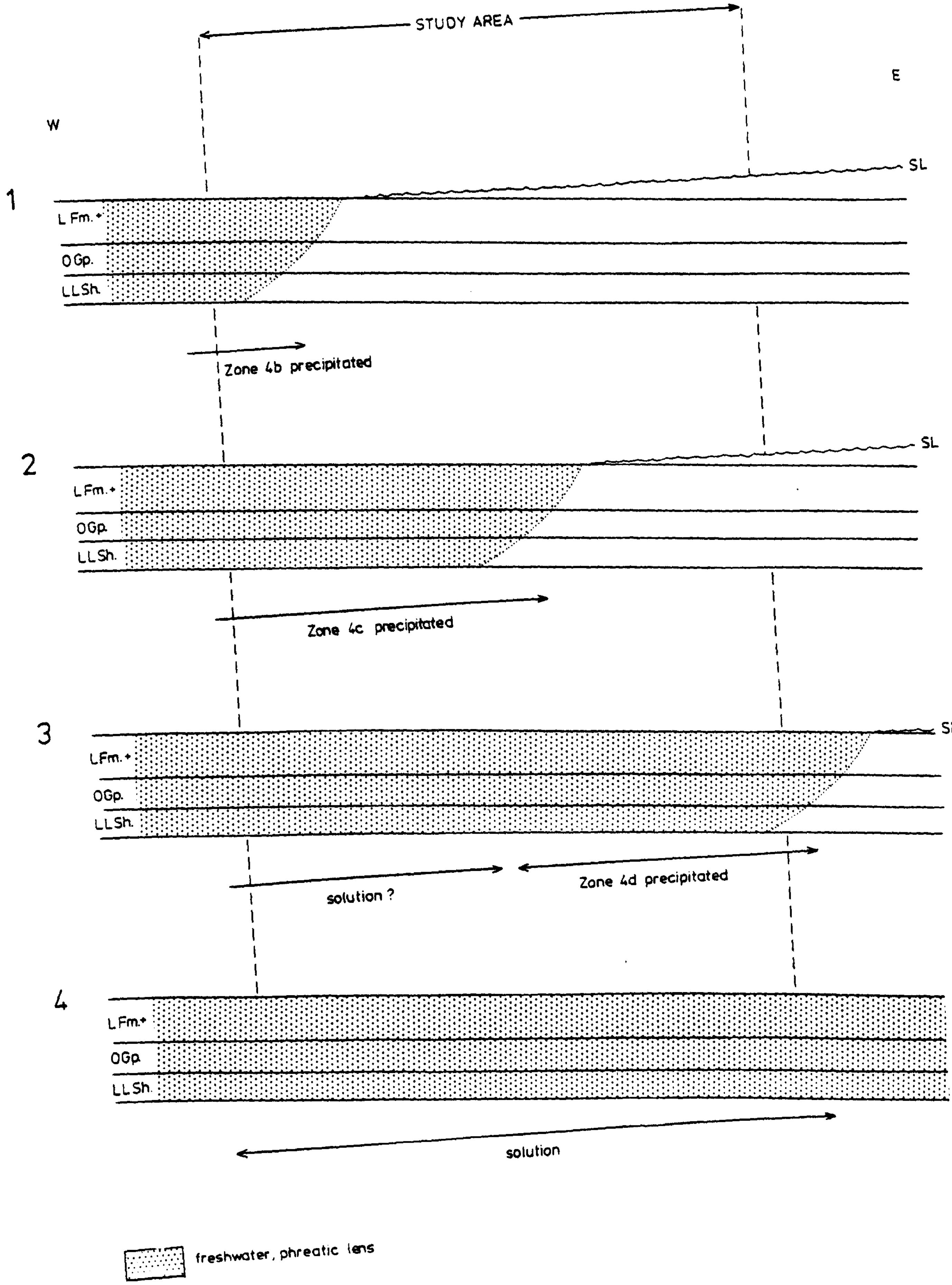
The Llanelly Fm. consists of peritidal deposits which contain many exposure surfaces; eleven have been identified by Wright (1981). Intermittent freshwater phreatic lenses must have existed within the Llanelly Fm. associated with these exposure surfaces. It is unlikely that these extended much, if at all, into the Oolite Group; this is explained by the Ghyben-Herzberg principle. Therefore, during Llanelly Fm sedimentation marine pore water resided within the Oolite Group sediments. The same may have been true during the deposition of the Dowlais Limestone, which is a dominantly subtidal unit, although it also contains exposure surfaces. If this is the case, it is unlikely that further cementation occurred until after the Dowlais Limestone was deposited. It has already been pointed out that Zones 4b-5 were precipitated, at the latest, in the mid-Carboniferous.

It is known that the volumes of water from which Zones 4b-6 were precipitated resided in the Llanelly Fm as well as the Oolite Group. Whether these waters were also present in the Dowlais Limestone and the Lower Limestone Shales can only be resolved by further work. It will be assumed that these waters resided in a large part of the Carboniferous Limestone.

The initiation of precipitation of Zone 4b-d cements moves progressively southeastwards, i.e. seawards, with time. This fits well with a model of precipitation during a marine regression (Meyers, 1978) (Fig. 8/5). Solution of Zone 4 cements (Solution Event 4) may have resulted when the sea had regressed far away from the Clydach area. Until it is possible to identify the absolute age of Zone 4 cements, it is impossible to identify the stratigraphic level at which this exposure occurred.

Fig.8/5 PALEOHYDROLOGY ASSOCIATED WITH THE PRECIPITATION OF ZONES 4b - d

Four diagrams show the progressive change in the position of the freshwater phreatic lens from which Zone 4b-d was precipitated. It progrades eastwards with time and is associated with a marine regression. It is assumed that the phreatic lens occuppied the Lower Limestone Shales, the Llanelly Formation and possibly overlying limestones as well as the Oolite Group.


STUDY AREA
W
E
1
SL
L Fm.+
OGp.
LLSh.
Zone 4b precipitated
2
SL
LFm.+
OGp.
LLSh.
Zone 4c precipitated
3
SL
LFm.+
OGp.
LLSh.
solution ?
Zone 4d precipitated
4
LFm.+
OGp.
LLSh.
solution
freshwater, phreatic lens

The model outlined in Fig. 8/5 and discussed above cannot be extended to Zones 5 and 6. Although they may well have been precipitated from pore waters that are meteoric in origin, their position in the phreatic lens is unclear. A few isolated isotope results indicate a marine influence in Zone 6 cements, suggesting that when these cements were precipitated the pore waters were in part marine. This is consistent with Zone 6 cements occurring in association with pseudomorphed gypsum.

The Clydach area

In Chapter 2 the study area was divided into two distinct diagenetic areas:-

AREA 1 : the Pwll-y-cwm and Blaen Onneu Oolites in the Clydach area, in which cement Zones 1, 2b and 6 are present. Dolomitisation is largely restricted to this area;

AREA 2 : the rest of the Oolite Group in which cement Zones 2a, 3, 4, 5 and 6 are present.

The isotopic distinctiveness of Area 1 was illustrated in Chapter 7.

Cement Zones 3 and 5 die out laterally into Area 1 over a distance of approx. ½ km. However, the vertical transition between Areas 1 and 2 is rapid, occurring over several metres. The presence of these two distinctive diagenetic areas suggests that the pore waters pervasive through most of the Oolite Group (Area 2) did not enter Area 1, which contained chemically distinct pore waters. This distinctiveness persisted until the precipitation of Zone 6 cement which is found in both Areas. However, despite the visual similarity between Zone 6 cements in both Areas they remain isotopically distinct. It is not understood why Area 1 was not affected by the hydrological changes occurring in Area 2.

It is not known whether Area 1 extends down into the underlying

Lower Limestone Shales in the Clydach Area. Whitcombe (1970) does not describe anything similar to the diagenesis seen in Area 1 in his description of the diagenesis of the Lower Limestone Shales.

The rare occurrences where the cement zones typical of Areas 1 and 2 are seen in association suggests that there was no precipitation of cement in Area 1 for a considerable period, spanning the precipitation of cement Zones 3 to 5 in Area 2. It is sometime during this period that dolomitisation occurred.

The above discussion is no more than a description of the distribution and diagenesis of Areas 1 and 2. It does not suggest how these two areas arose or how they remained distinct for such a considerable period. Some of the problems associated with Area 1 are considered and discussed below. The discussion is, however, speculative and it is difficult to draw firm conclusions.

Why was there no precipitation of calcite in Area 1 while cement was being precipitated in Area 2?

The lack of precipitation of calcite in Area 1 probably has many possible explanations. Some are suggested below:

1. for the period spanning the precipitation of cement Zones 3 to 5 the pore water in Area 1 was undersaturated with respect to calcite. There is no evidence of solution during this period and, indeed, dolomitisation occurred suggesting that for at least some of that time the pore waters were supersaturated;
2. the pore waters in Area 1 were 'stagnant' and there was no transport of carbonate into the area, thus preventing cementation. Stagnation would have resulted from the paleohydrological nature of the area rather than to a restriction of flow of the pore waters due to low permeabilities;

3. the carbonate supplied to the area was used up in dolomitisation and the precipitation of dolomite cement rather than the precipitation of calcite.

Why do the pore fluids in Areas 1 and 2 stay separate?

Area 2 is typified by constantly changing pore fluids, described earlier in this chapter. However, there is no evidence that the pore waters in Area 2 ever dislodged those in Area 1, at least not until Zone 6 precipitation. There is not even much evidence of mixing between the two. The transition between Areas 1 and 2 is wider laterally than vertically. The lack of mixing between the two pore waters suggests that Area 1 has distinct physical parameters. For instance, the pore waters in Area 1 may have been denser than those in Area 2. It rests on the impermeable shales that make up the top of the Lower Limestone Shales at the down-dip end of the outcrop. This is the lowest possible position that such pore fluid could take up in the Oolite Group of the study area. Of course the study area cannot be considered in isolation. Since the distribution of Area 1 outside the study area is not known no firm conclusions can be made.

What effects did Area 1 have on the precipitation of cements in Area 2?

In the east of the field area the pore waters of Area 2 rested abruptly on those of Area 1. The Zone 5 cements that lie near the edge of Area 1 consist of alternating ferroan and non-ferroan second-order zones. The number of alternations decreases with increasing distance from Area 1 (Fig. 2/24). At Pwll du Zone 5 consists of alternating ferroan and non-ferroan second order zones throughout the entire thickness of the Gilwern Oolite. The rise in the level at which Zone 5 consists of alternating second order mimicks the rise in the level at which dolomitisation occurs. Just to the east of Pwll du the entire thickness of the Oolite Group is dolomitised (Fig. 8/6).

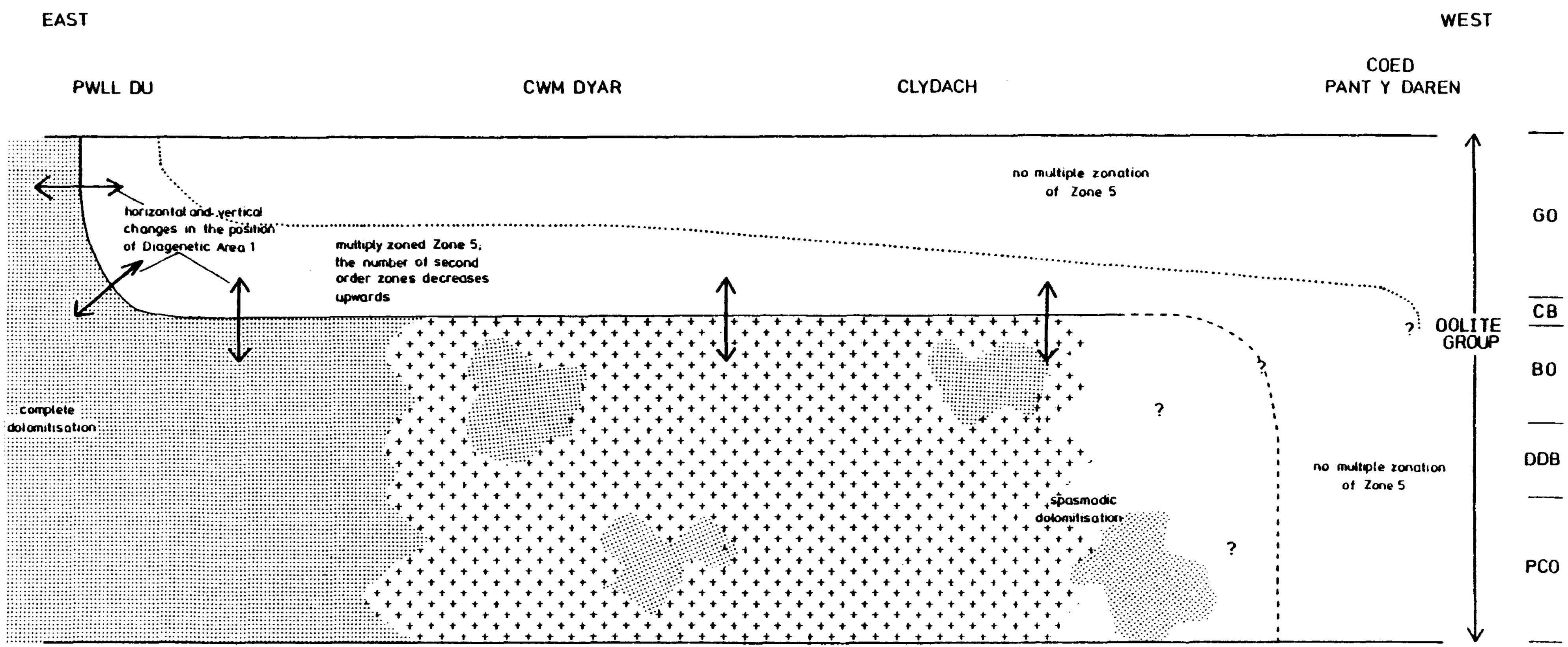
The close association of the Zone 5 cements consisting of alternating second order zones with Area 1, suggests that the origin of their zonation is in some way controlled by the pore fluids in Area 1. It is thought that the development of Zone 5 cements displaying second order zonation resulted from an oscillation in the position of Area 1 pore fluids. At the eastern end of the study area both vertical and lateral movements of Area 1 could occur due to the upturn in Area 1 (Fig. 8/6). This is consistent with the Zone 5 calcite containing most second order zones at the eastern end of the outcrop. No second order zonation was found at the western end of Area 1. This may be the result of the greater mixing having occurred at this end of Area 1.

The nature of the interaction between Areas 1 and 2 is not known. It may be in the form of the mixing of the two pore fluids.

What is the nature and origin of the pore fluids that affected Area 1?

There is conflicting evidence as to the nature of the pore waters in Area 1. The diagenetic events recorded suggest that the pore waters changed during diagenesis. The initial event, pyrite precipitation, must have occurred in a reducing SO_4^{2-}-rich environment. However, there is also ample evidence of the early interaction of the area with meteoric waters:

1. solution of aragonite fossils;
2. precipitation of intensely ferroan calcite (requires reducing, SO_4^{2-}-free waters);
3. negative $\delta^{18}O$ values in Zones 1 and 2 (see Chapter 7).



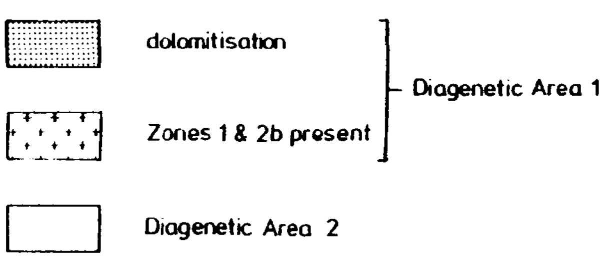


Fig.8/6 PALEOHYDROLOGY OF DIAGENETIC AREA 1

Diagenetic Area 1 contains cement Zones 1 and 2b. Also dolomitisation is largely restricted to it. The amount of dolomitisation decreases westwards. In Diagenetic Area 2 cements close to Diagenetic Area 1 have a multipully zoned Zone 5. The number of second order zones increases towards Diagenetic Area 1. It is thought that this may be associated with an oscillation in the position of the boundary between Diagenetic Areas 1 and 2(arrows). At Pwll du there is an upturn in Diagenetic Area 1 which is associated with Zone 5 cements in Diagenetic Area 2 being multipully zones throughout the entire thickness of the Gilwern Oolite.

Although $\delta^{18}O$ values indicate the influence of meteoric waters, the $\delta^{13}C$ values indicate the strong influence of marine carbonate sources, perhaps from the allochems of the area in question. Large amounts of meteoric water with low $\delta^{13}C$ values resulting from the influence of light soil gas CO_2 have not passed through Area 1, as they have in Area 2. The isotope values of Zone 6 vary between Areas 1 and 2, although they are petrographically similar. This again is attributed to re-equilibration of the pore waters that precipitated Zone 6 with an unaltered marine carbonate reservoir in Area 1.

Area 1 is the most northerly extent of the dolomitisation that affects the eastcrop of the Lower Carboniferous Limestone in South Wales. It has been demonstrated that dolomitisation occurred between the precipitation of Zones 2b and 6 (Chapter 4, Fig. 4/1). Although it is generally presumed that high salinities are necessary to produce dolomitisation, this is not necessarily the case (Folk & Land, 1975). Relatively high Mg/Ca ratios can be produced in low salinity pore waters by the mixing of meteoric and marine pore waters. However, transport of substantial amounts of Mg^{2+} is required. The isotope data is inconclusive in indicating the nature of the pore waters causing dolomitisation. The $\delta^{13}C$ results have marine values, but the $\delta^{18}O$ values can be interpreted in many ways.

Hypersaline dolomitising brines would fit well with the suggestion that the pore fluids in Area 1 had high densities. However, the evidence that the early diagenetic events resulted from the influence of meteoric water means that, at least initially, the pore fluids in Area 1 were not hypersaline. A mixing-zone model is consistent with the nature of the diagenesis of Area 2 (precipitation of Zone 4 during a marine regression). However, the distribution of Area 1 and the regional extent of dolomitisation suggests that this hypothesis is unlikely.

Dolomitisation does not extend to the most westerly extent of Area 1; it dies out rapidly between Cwm Dyar and Clydach, although small areas further west show spasmodic dolomitisation. It would seem that the pore waters at the western end of Area 1 did not have such a high dolomitising potential as those further east. Two possible reasons are suggested below:

1. mixing of the pore waters of Area 1 with the meteoric waters of Area 2 caused a reduction of the Mg/Ca ratio that was sufficient to inhibit dolomitisation;
2. the pore waters in Area 1 were isolated from the Mg^{2+} source since there was no through-flow of water. Without replenishment of Mg^{2+} , effective dolomitisation could not occur.

The position of Area 1 suggests that the pore fluids affecting it were introduced laterally, from the east, perhaps sinking down from higher levels east of Pwll du (N.B. dolomitsation rises here to include all of the Oolite Group). There is no evidence to suggest that the pore waters affecting Area 1 ever passed through Area 2. The form of Area 1 suggests that a lobe of pore waters different to those in Area 2 extended up-dip, under Area 2, in the Clydach area.

There are many problems associated with the interpretation of the paleohydrology in the Clydach area, not the least being the lack of data available on which to base an interpretation. Many questions about the area remain unanswered. An extension of the study area eastwards and trace element data from the cements are essential in understanding the paleohydrology of this area.

8.4 Future Work

Throughout the text suggestions have been made where it is thought that further work would be useful. Topics that would benefit from further investigation fall into two categories:

1. those pertaining to the understanding of the diagenesis on a regional scale;
2. isolated topics associated with details of the diagenesis.

Topics falling into category 1 include:

a. an extension of the area over which the cement zones identified in the study area can be correlated, both vertically and laterally, in an attempt to work out the spatial distribution of former groundwater bodies and their absolute age;

b. microprobe analysis of the cement zones that have been identified, especially for Mn^{2+}, Fe^{2+}, Mg^{2+}, and Sr^{2+} in an attempt to:-

   1. identify the nature and origin of the pore fluids from which the cements were precipitated;
   2. correlate the trace element chemistry with the intensity of the CL and deduce the relationship between Mn^{2+} and Fe^{2+} content and CL;
   3. correlate the trace element chemistry with the crystallographic form and changes in the form of the cements;

c. fluid inclusion study of the cements to find the temperature and depth at which they were precipitated. Once this is known the $\delta^{18}O$ of the pore waters from which the cements were precipitated can be calculated;

d. isotope analysis of the allochems from the Lower Limestone Shales and the Llanelly Fm. to see if the trend seen in the allochems of the Oolite Group is continued in these or not.

Topics falling into category 2 include:

a. serial sectioning of crystals showing 'Fir-tree' zonation to accurately work out the distribution of the two ferroan calcites involved and hence to work out an accurate model for the formation of this type of zonation;

b. SEM examination of the fibrous crystals found within the Daren Ddu Beds and Zone 2a cements;

c. to simulate the growth of calcite cements in which the crystallographic form changes many times to see how this affects the shape of inter-crystalline boundaries.

APPENDIX A

CATHODOLUMINESCENCE

Cathodoluminescence forms an important part of this study and CL photographs are widely used. Due to the variety of machines in use and the various photographic techniques employed in recording CL information it is important to record the conditions under which photographs are taken for comparitive purposes (Marshall, 1977). This is done below:

Sample Preparation

Thickness:	20–50 µm.
Surface:	polished with 2 µm. alumina

Instrument Parameters

Model:	the instrument used is housed and was built in the Department of Geology at Nottingham University
Beam energy:	30 kV DC
Beam current:	4 – 6 mA
Spot size:	the spot size can be varied with a solenoid. The usual working diameter is approx. 2 mm.
Ambient gas:	air
Gun type:	cold cathode

Photographic Conditions

Microscope:	Zeiss photomicroscope 11 with a vertical photo tube so that all the light from the specimen can be used.
Objective:	Leitz Pl 2.5/0.08
	Zeiss Neofluar 6.3/0.20
Magnification:	x 7 to x 56
Camera:	Leitz
Film type:	Ilford HP5
Exposure time:	average 1 min. (range ½ to 2 mins.)
Processing:	developed in Acutol for twice the recommended time.

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