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Meteoric phreatic diagenesis in cyclic late Dinantian carbonates, northwest England

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Abstract

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Luminescent/non-luminescent zoned syntaxial overgrowths in carbonate grainstones of late Asbian (late Dinantian) age of the southern Lake District represent precipitation in barely saturated, relatively shallow (15–120 m), meteoric phreatic pore waters. The zonation reflects repeated establishment of meteoric lenses, in response to eustatic effects, within cyclic carbonate platform sediments isolated from sources of laterally-fed groundwaters. Geochemistry and petrology suggest that there was a consistent positive covariance between Eh of pore waters and precipitation of calcite during establishment of these lenses, such that cements only precipitated from suboxic and oxic meteroic waters. Mixing-zone and stagnant marine phreatic diagenetic environments are thought to have been sites of non-precipitation to slight dissolution. Cement cycles can be correlated up to 30 km across the platform and decrease in number, in a predictable fashion, up through the sequence. The stratigraphic resolution they offer within this platform is more sensitive than that of microfossils in the same sequence. Cementation patterns are more complex in the outer 5 km of the platform and increase in complexity basinwards, reflecting: the influences of lowstand sea levels; locally developed erosional and depositional slopes; lateral components within meteoric flow patterns; rapid lateral facies variations and possible trace element partitioning. The base of the meteoric lenses from which these cements precipitated was controlled by the presence of a shale aquitard. This style of cementation ceased after an early Brigantian platform drowning event.

Introduction

The use of staining and cathodoluminescence to reveal zoning of cements in carbonate rocks is well documented. Early studies were principally descriptive (Dickson, 1966), but later work has aided the interpretation of carbonate diagenesis in a variety of geological settings and on various scales. In the field of meteoric diagenesis, large scale, laterally-sourced groundwater systems, in which cements may be correlated over large distances, have been documented by Meyers (1974, 1978), Grover and Read (1983) and Doborek (1987). Studies on reefs and buildups (Frykman, 1985, 1986) have revealed some of the hazards of correlating cements and the importance of local diagenetic environments. Emery and Dickson (1989) demonstrate how a small meteoric lens developed during local emergence, whilst work on large-scale cyclic sequences, in which meteoric water is repeatedly sourced from successive overlying emergent surfaces, forms a fourth group of studies (Berry, 1984; Walkden and Berry, 1984a; Walkden, 1987; Horbury, 1987; Goldstein, 1988).

We intend to demonstrate how meteoric cements vary through a 100 m thick unit of cyclic

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carbonate platform deposits and how these cements may be correlated across the platform. Variations in cement stratigraphy occur near to the platform edge and these are discussed. An extensive database of 700 thin sections and 3000 acetate peels, combined with the results of work on both depositional environments and other diagenetic fabrics, has enabled us to interpret these cements within an integrated diagenetic/depositional model developed for the 30 km wide study area. Such cements form only a small proportion of the diagenetic sequence, under 1% by volume, but are of interest as indicators of positively covarying Eh and calcite saturation and, also, because of their intimate association with depositional processes on an isolated carbonate platform subjected to sea level changes.

Regional geology

The cements described here are from the upper part of the Urswick Limestone Formation in South

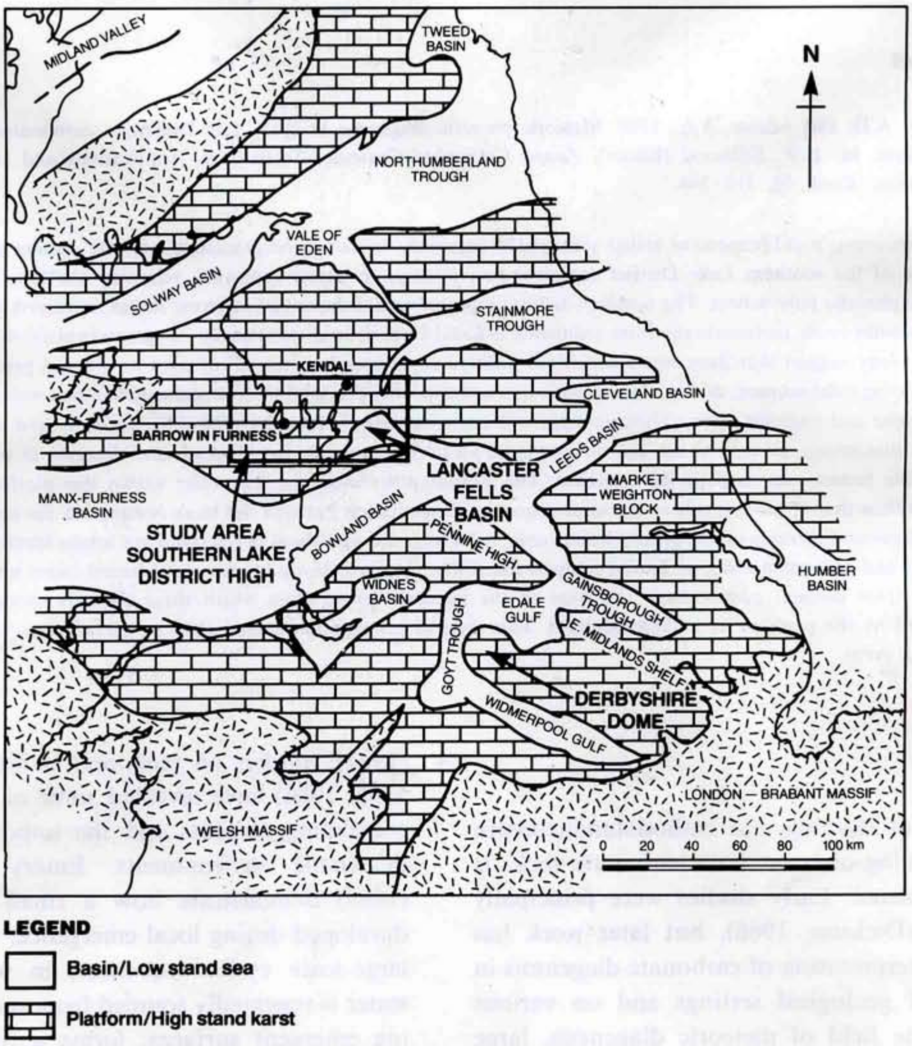


Fig. 1. Late Asbian palaeogeography. The majority of platforms are isolated, and are separated by deep water "troughs" and "gulfs". Therefore, meteoric diagenesis during emergent events usually represents a relatively closed system. Modified after Fraser et al. (1990).

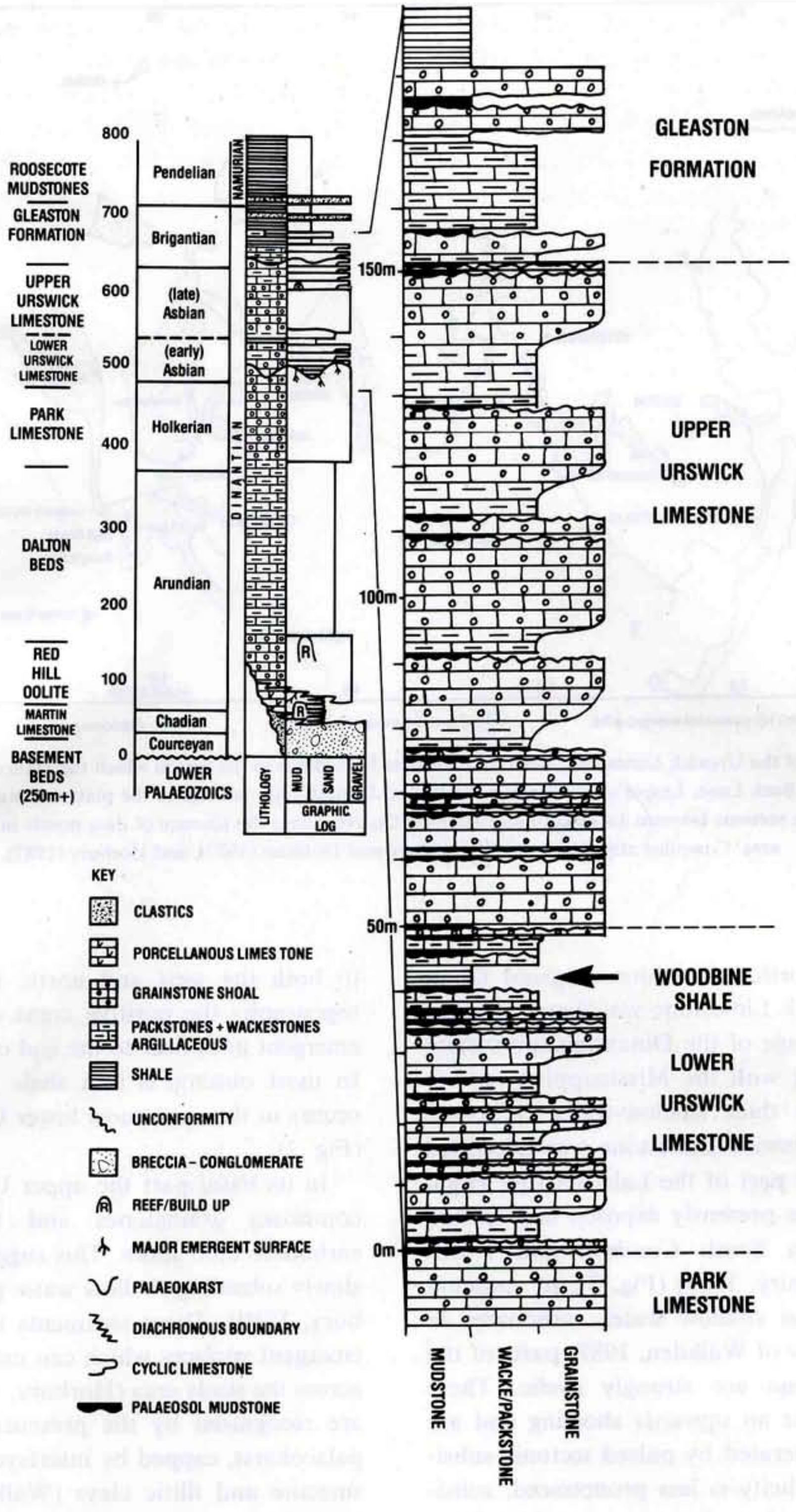


Fig. 2. Summary Dinantian and Asbian stratigraphies in South Cumbria and North Lancashire. Note the grainstone sequence at the base of the upper Urswick Limestone in which the best developed overgrowths occur, the packstone/wackestone to grainstone cycles above, with which the overgrowths are intimately related, the Woodbine Shale aquitard and the mudstones in the Gleaston Formation which represent a Late Dinantian drowning event. After Rose and Dunham (1977) and Horbury (1989).

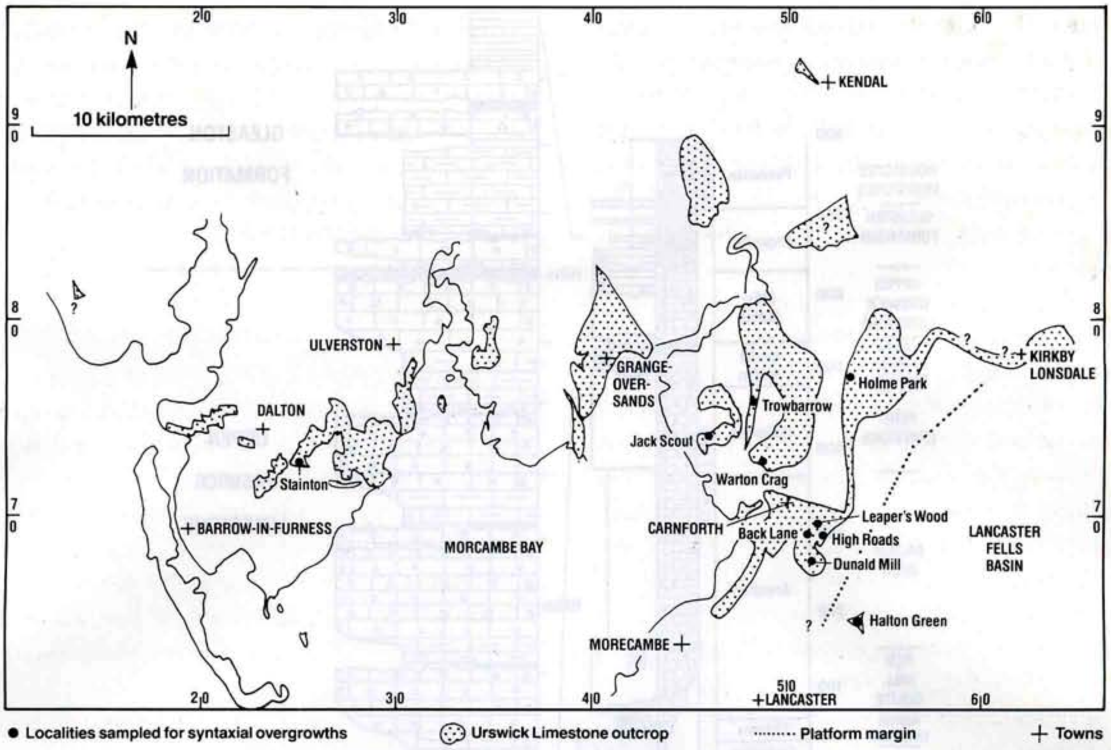


Fig. 3. Outcrop map of the Urswick Limestone. Note the Lancaster Fells Basin to the east in which the Halton Green outcrop occurs and the proximity of Back Lane, Leaper's Wood, High Roads and Dunald Mill quarries to the platform margin. There are no well exposed and complete sections between Jack Scout and Stainton Quarry, hence the absence of data points in the centre of the study area. Compiled after Garwood (1913), Rose and Dunham (1977), and Horbury (1987).

Cumbria and North Lancashire, England (Figs. 1–3). The Urswick Limestone was deposited during the Asbian stage of the Dinantian sub-system (broadly equating with the Mississippian) and is part of a 500 m thick shallow-water carbonate sequence. The Urswick Limestone was deposited over the southern part of the Lake District High, comprising all the presently exposed area of Dinantian rocks in South Cumbria and North Lancashire (Horbury, 1989) (Fig. 3). In common with other Asbian shallow water carbonates in Britain (see review of Walkden, 1987) parts of the Urswick Limestone are strongly cyclic. These cycles demonstrate an upwards shoaling and are thought to be generated by pulsed tectonic subsidence. Where cyclicity is less pronounced, subsidence is thought to have been more gradual (Horbury, 1989).

The lower Urswick Limestone onlaps the underlying Park Limestone (Horbury, 1989) (Fig. 2) to both the west and north, infilling an earlier topography the positive areas of which remained emergent until near to the end of the early Asbian. In most outcrop a thin shale (Woodbine Shale) occurs in the uppermost lower Urswick Limestone (Fig. 2).

In its basal part the upper Urswick Limestone comprises grainstones and thin porcellanous carbonate mudstones. This suggests a steadily but slowly subsiding shallow water platform top (Horbury, 1989). These sediments are punctuated by emergent surfaces which can usually be correlated across the study area (Horbury, 1989). The surfaces are recognised by the presence of mammillated palaeokarst, capped by interlayered illite-smectite, smectite and illitic clays (Walkden, 1972, 1974). Such surfaces are thought to represent glacio-eustatic regressions during which sea level falls were rapid. After marine conditions became re-established, similar facies developed as prior to emergence such that the overall shallow marine character of the carbonates was only temporarily interrupted (Horbury, 1989).

The upper part of the upper Urswick Limestone is more strongly cyclic than the lower part, with facies sequences comprising argillaceous sub-wavebase packstones and wackestones capped by cycle-top shoal grainstones. Four 10–15 m thick cycles are developed, these represent periods of rapid tectonically-controlled subsidence followed by upwards shoaling in response to sedimentary processes. Several emergent surfaces are often developed within the grainstones at the top of each shoaling cycle. These emergent surfaces are thought to represent continued glacio-eustatic regression. As in the lower part of the upper Urswick Limestone, after glacio-eustatic transgression, similar facies developed as prior to emergence, except where emergence was interrupted by rapid tectonic subsidence (Horbury, 1989).

At localities south of Carnforth (Fig. 3) sediments change in character and a range of features indicative of a platform margin are found. These include small algal reefs and extensive grainstone shoals with spillover lobes. Basinal equivalents are found near Halton Green, these comprise debris flow breccias and turbidites (Horbury, 1987, 1989). The overlying Gleaston Formation, of Brigantian age (Rose and Dunham, 1977) (Fig. 2), comprises shoaling cycles at the base, passing up into a sequence dominated by basinal siliciclastic mudstones.

Methods

Polished thin sections were examined using a Technosyn Cathode Luminoscope model 8200 Mk II with operating conditions of 14–15 kV beam energy, 0.5 mA beam current and a vacuum of 50–60 mT. Photographs were taken using Ilford XP-1 film with a standard exposure time of 2 minutes.

Some cements were analysed for selected trace elements using an electron microprobe. Doubly polished thin sections were carbon coated and analysed in a Camebax Cameca microprobe, operating in a wavelength-dispersive mode, with a beam current of 2.4 nA at a voltage of 15 kV and a beam diameter of 10 μm. The livetime for analysis was 80 seconds. The detection limits were approx. 150 ppm for Fe and approx. 120 ppm for Mn. The beam diameter of the wavelength-dispersive mode used did not allow detailed sampling of individual cement zones, so conclusions are based upon semi-quantitative data.

Early diagenesis

The zoned syntaxial overgrowth cements which are the subject of this paper post-date a number of other diagenetic features summarised below, in their paragenetic sequence.

(1) Isopachous fringes of equant calcite and locally developed overgrowths on echinoderms (Fig. 4a). These occur in laterally impersistent and vertically restricted zones and in intraclasts. They are interpreted as marine cements, associated with local omission surfaces.

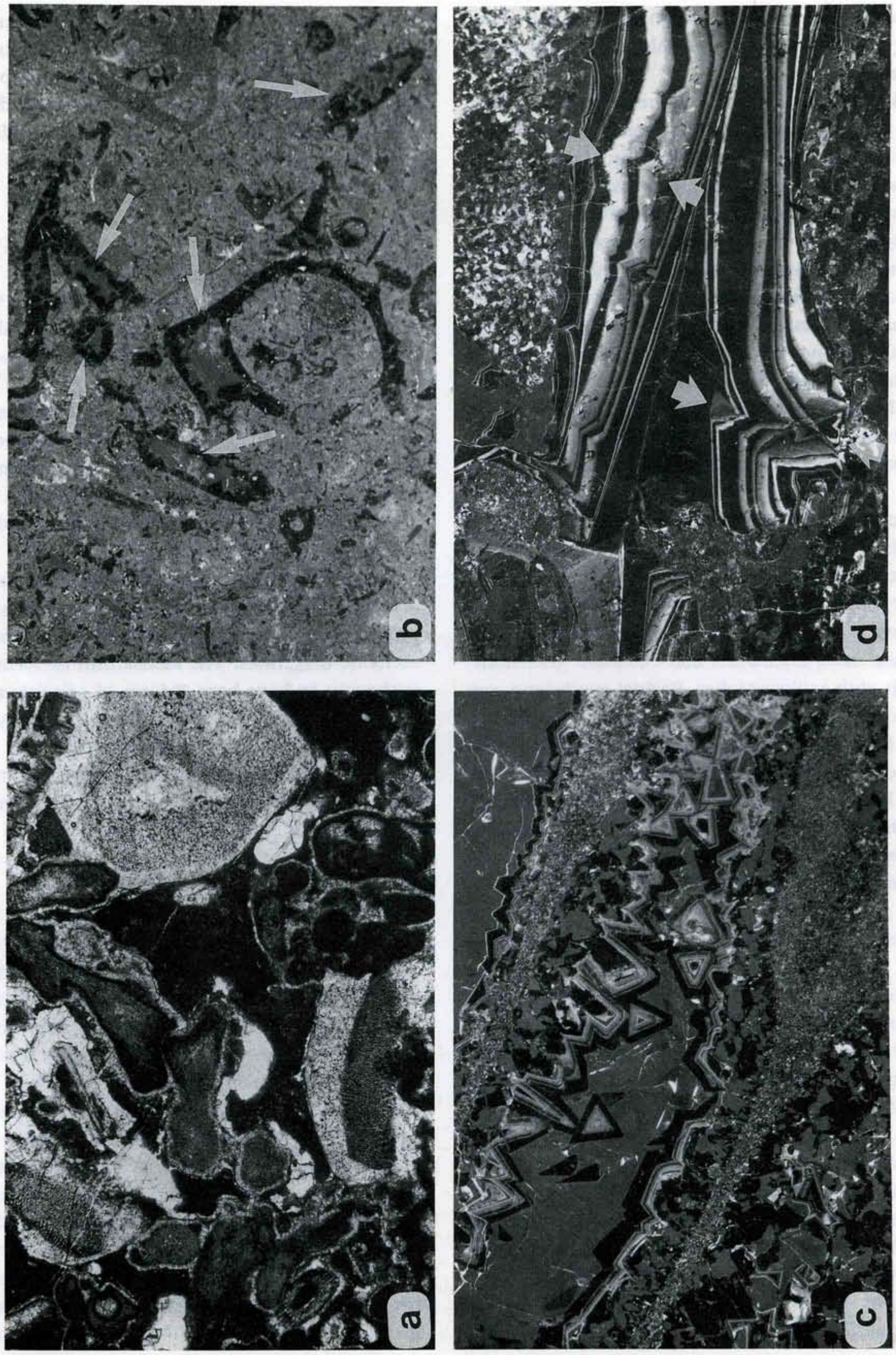
(2) Precipitation of fine calcite spar in burrows (Fig. 4b). The spar probably originated via stabilisation of lime mud during marine or earliest meteoric diagenesis. The mechanism of formation is thought to have been a form of solution-reprecipitation, similar to that described by Steinen (1982) (Horbury, 1987).

(3) Pedogenic fabrics such as rhizocretions, alveolar texture, needle-fibre calcite and laminar calcrete.

(4) Dissolution of aragonitic allochems (Fig. 4b).

(5) Precipitation of several types of early meteoric cements. These consist mostly of euhedral crystals up to 500 μm in length that fill interganular, mouldic (Fig. 4b) and intragranular (Fig. 4c) porosity, line rhizocretions and are often associated with emergent surfaces.Typically these cements are non-luminescent, but in some cases contain multiple, thin luminescent zones, which have smooth, well-defined contacts with the non-luminescent cement zones (Fig. 4c). They resemble the caliche cements described from the Asbian of North Wales by Solomon and Walkden (1985).

Syntaxial overgrowths on large, monocrystalline substrates in the lower Urswick Limestone reveal a similar zonation to the nearby non-syntaxial meteoric cements. These cements comprise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sub-parallel growth zones and do not usually show any dissolutional events (Fig. 4d). The zonal sequence is usually consistent within one thin section, but correlation of zones between thin sections from different horizons at one locality or between localities is rarely possible. These cements are believed to have developed in response to lateral water flow, possibly from a permanent meteoric source such as the exposed Park Limestone which was being onlapped during deposition of the lower Urswick Limestone. They resemble in appearance and, by analogy, are thought to be similar in origin to those described by Meyers (1974, 1978), Grover and Read (1983) and Doborek (1987).

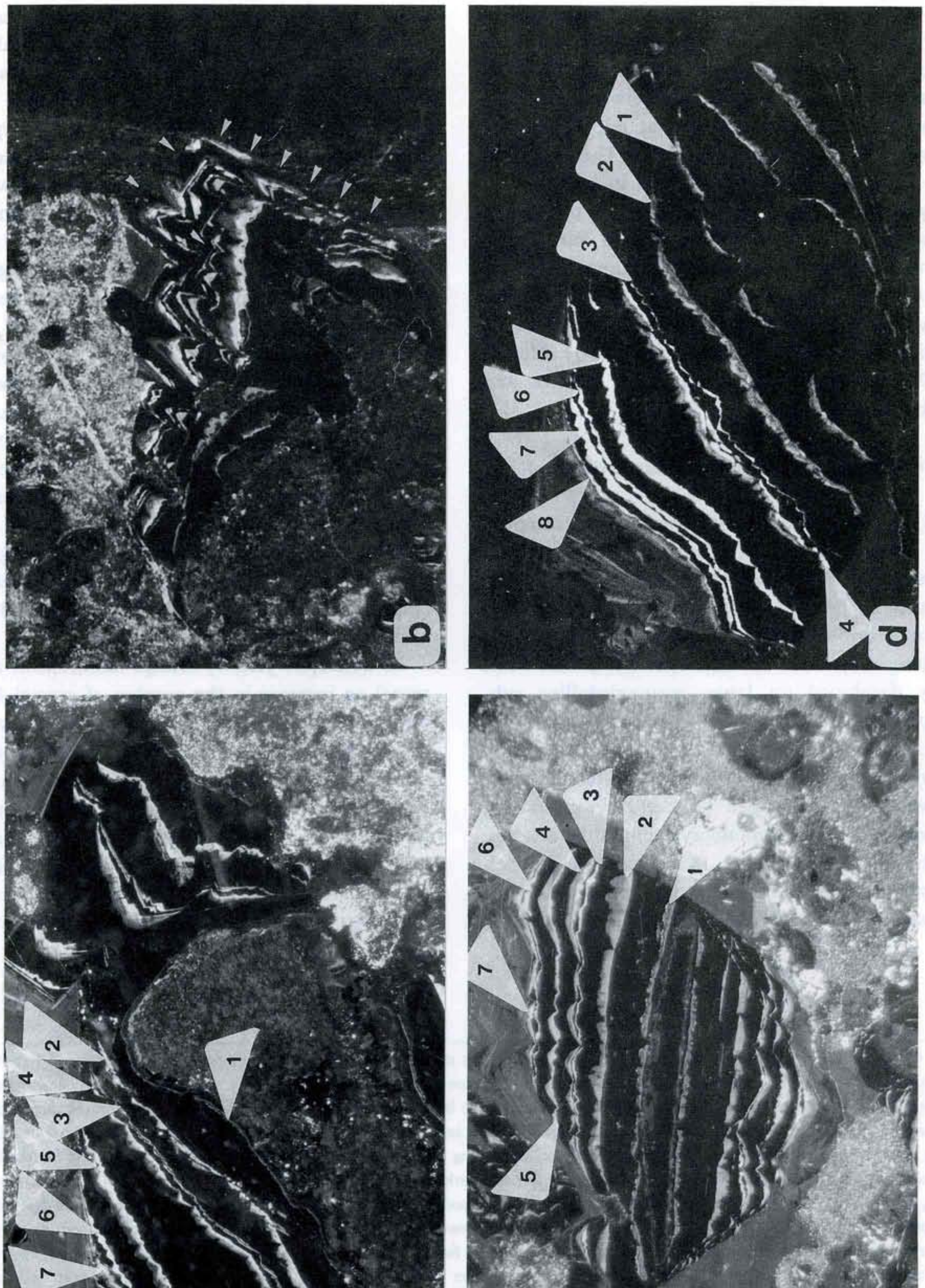
Correlatable zoned syntaxial overgrowths

Cements showing luminescent zoning comprising alternating yellow, orange and non-luminescent (black) calcite, which can be correlated from locality to locality, post-date the diagenetic features described previously. They occur in the form of limpid syntaxial overgrowths 0.1–2 mm wide, only developed on large, monocrystalline substrates (Fig. 5a, b). They comprise less than 1% of the total rock volume. Substrates are commonly unmicritised crinoidal debris, although overgrowths also developed on earlier overgrowths, echinoid spines and monocrystalline tubular algae such as *Kamaena* and *Kamaenella* (Fig. 5c). Growth is preferential in the direction of the substrate crystallographic *c*-axis (Fig. 6a, b) and is thus similar to the overgrowths described by Evamy and Shearman (1965, 1969) and Walkden and Berry (1984b). Away from the substrate, crystals develop an overall more euhedral form and are identical in appearance to the type C contouring overgrowths described by Walkden and Berry (1984b, their figs. 2c and 3a). Growth was as simple pore-fills with no evidence of grain displacement using the criteria of Maliva (1989) since these overgrowths grow around obstructing grains (Figs. 6c, d; 7a, b). But in other instances the nuclei do appear to "float" within cement (Fig. 5c) which is taken to indicate locally high (approx. 40%) porosity at the time of cementation. Correlatable overgrowths are well developed in the upper Urswick Limestone platform deposits. They are very rare in the lower Urswick Limestone, are absent from basinal facies and from the Gleaston Formation. At localities close to the inferred platform edge, overgrowths of similar morphology are present, but display a more complex zonal scheme (Fig. 5b). These overgrowths are considered separately later in the text.

In detail the yellow/orange luminescent zones reveal an increase in the number of crystal facies developed compared to the non-luminescent calcite on which they precipitate (Fig. 6c, d). The overall development of euhedral crystals was, therefore, achieved by alternation of multiple nucleation followed by growth into simple, more euhedral forms.

Overgrowths are best-developed in crinoidal/peloidal grainstones which occur at the base of the upper Urswick Limestone. They are present, al-

Fig. 4. (a) Pore lining isopachous marine cements and equivalent thick syntaxial cements developed on echinoderms in late Asbian grainstones, Dunald Mill Quarry. A later generation of vadose meteoric micrite infills porosity and emphasises the earlier cement. Plane polarised light, field of view 2 mm, Dunald Mill Quarry. (b) Burrow fill cements. This wackestone was stabilised during marine or earliest meteoric diagenesis, resulting in the orange to brown luminescent fine calcite spar which forms the bulk of the field of view. Former aragonitic bioclasts (arrowed) were dissolved during meteoric diagenesis and their moulds were infilled with shallow meteoric, non luminescent (black) followed by slightly ferroan, dark brown to grey luminescent burial cements. Cathodoluminescent light, field of view 2 mm, Trowbarrow Quarry. (c) Shallow meteoric non- and yellow-orange-brown luminescent euhedral pore-fill cements. Here these infill intragranular porosity in a coral and demonstrate a complex zonal sequence. The final cement generation is a dark brown luminescent burial cement. Cathodoluminescence, field of view 2 mm, Trowbarrow Quarry. (d) Non-yellow/orange luminescent syntaxial overgrowth of the type restricted to the lower Urswick Limestone. Note the generally regular pattern of cement growth with no dissolutional hiati, no fretted growth forms and the propogation of irregularities in growth bands through the sequence (arrowed). These cement sequences can be traced into nearby pore-fill cements such as (c) and represent precipitates of laterally sourced shallow meteoric lenses. Cathodoluminescence, field of view 2 mm, Middlebarrow Quarry.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though comparatively poorly developed and less numerous, in the upper parts of younger shoaling-upwards cycles. Overgrowths are rare in cycle base packstones and wackestones and absent from porcellanous micritic limestones present at the very top of cycles. They pre-date both regionally extensive, grey to orange-brown luminescent, slightly ferroan cements, of probable burial origin and grain-to-grain pressure solution (Horbury, 1987). The zoned overgrowths are always non-ferroan, as revealed by staining with potassium ferricyanide; the threshold for visual recognition of ferroan calcite being approximately 0.5 mole wt.% Fe or 10,000 ppm (Lindholm and Finkelman, 1972). Electron microprobe analyses on selected samples revealed no iron above the detection limit of 150 ppm, whilst manganese was present at concentrations of up to 870 ppm, although typical values were in the range 150–300 ppm in the luminescent calcite.

Cementation cycles

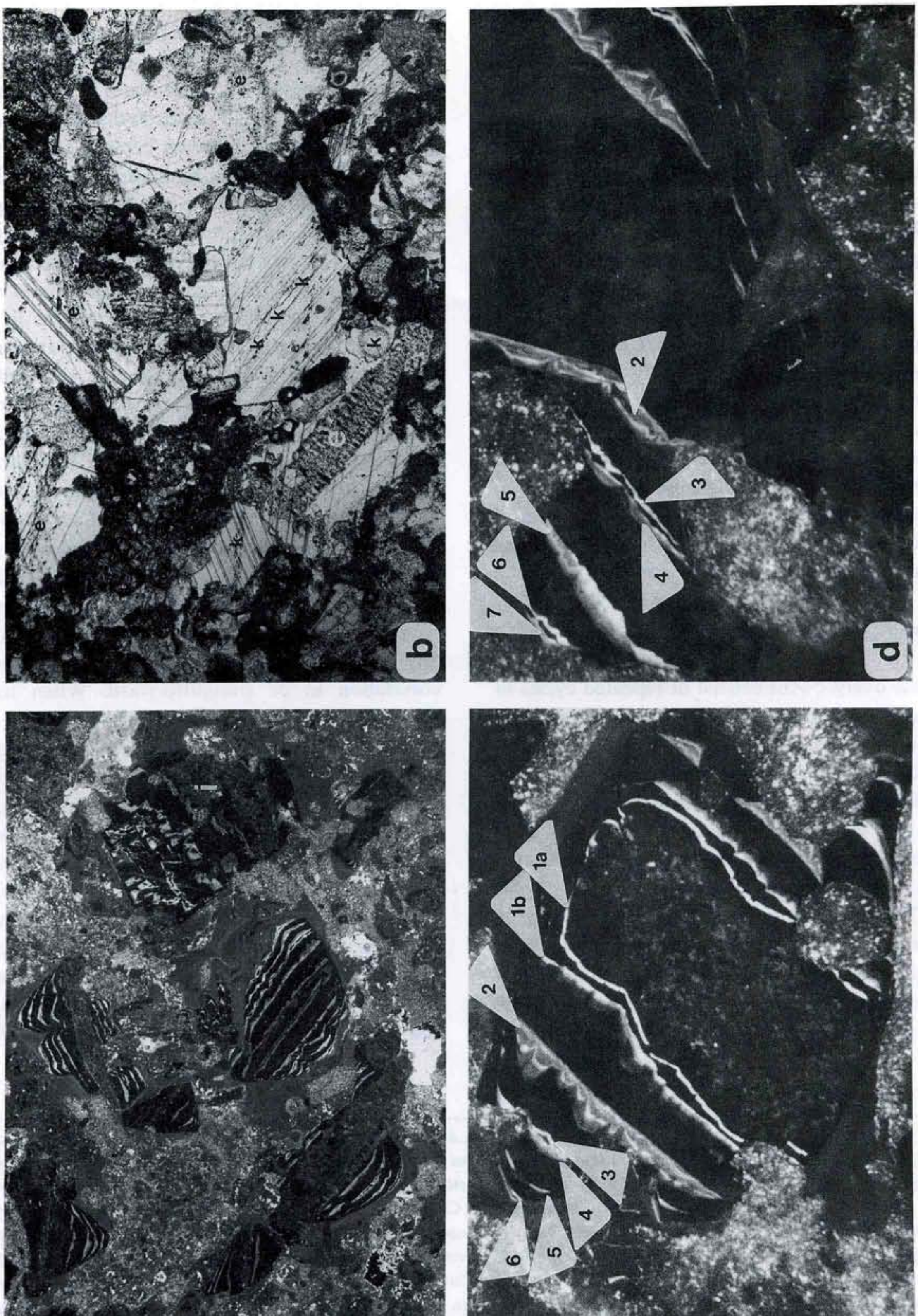
These overgrowths consist of repeated cycles of cement which, when well developed, occur as sequence of yellow or orange followed by non-luminescent (black) calcite. Cement cycles are bounded by well-defined, sharp breaks which represent the initiation of many crystal facies on a simple substrate and in some cases dissolutional events (Figs. 5a, c, d; 6c, d).

In 76% of samples studied there is no change in luminescent colour across the luminescent zone. However, in 23% of samples studied the yellow luminescent zone changes to orange in a gradational or stepwise manner outwards. In only 1% of samples was there a change from orange to yellow outwards (Fig. 8). The luminescence colours and relative thicknesses of colour zones in each cement cycle are similar for all overgrowths, with the most obvious differences between cement cycles being in the thicknesses of non-luminescent cement. Each cement cycle is distinctive and cycles are sequentially developed in a predictable sequence (Fig. 8). The same sequence is developed in all overgrowths in a thin section (Fig. 6a). Thin sections in close proximity have similar cement sequences in well developed overgrowths (Figs. 5c, 7b). Individual overgrowths may not demonstrate the full sequence as the result of: (a) the plane of section not cutting the earliest formed zones, or (b) because the later zones were growing out of the plane of section, or (c) because the overgrowths occupied all the available space early during their growth.

Therefore composite, idealised sequences were reconstructed for some samples (Fig. 6a, c, d).

The characteristics of individual cement cycles vary slightly within and between thin sections in any given locality, but are sufficiently similar for correlation to be straightforward. When traced upwards through the stratigraphic sequence it is apparent that there is a successive disappearance of the basal cement cycles, such that by the top of the Urswick Limestone this type of syntaxial overgrowth is absent (Figs. 5c; 7b–f). This enables the cements to be used as stratigraphic markers with a resolution better than that provided by microfossils *in the same sequence*, such that five or six divisions of the upper Urswick Limestone can be achieved, representing one foraminiferal biozone. For each locality a "typical" overgrowth sequence can be selected, preferably from the base of the

Fig. 5. (a) Syntaxial overgrowth of the platform variety. This example demonstrates well the development of characteristic yellow/orange/non-luminescent cement cycles (labelled). Subzones within the luminescent parts of cement cycles define euhedral growth patterns, whilst the bases of cycles are more irregular and etched in appearance. Note the similarities with Figs. 5c, d; 6c, d and 7a. The final pore-fill is a brown luminescent burial cement. Cathodoluminescence, field of view 2 mm, Stainton Quarry. (b) Syntaxial overgrowth of the platform margin variety. The zonal sequence is distinctly more complex than in (a) and this example shows evidence of later pressure-solution against a brachiopod (arrowed). The final pore-fill is a brown luminescent burial cement. Cathodoluminescence, field of view 1 mm, Back Lane Quarry. (c) Platform-type syntaxial overgrowth nucleated on a fragment of the alga *Kamaenella*. There is a distinctive zonal sequence as observed in Figs. 5a, d; 6c, d and 7a. In this example the nucleus appears to float in cement, but it may be supported out of the plane of the section. The overgrowth is, therefore, probably not of the displacive type. Cathodoluminescence, field of view 1 mm, Trowbarrow Quarry. (d) Zone sequence from Warton Crag. Note the similarities with Figs. 5a, c; 6c, d and 7a. Cathodoluminescence, field of view 1 mm, Warton Crag.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upper Urswick Limestone, where the sequence contains all possible cycles (Figs. 5a, c, d; 6c, d; 7a). When these sequences are compared the similarity across the platform is remarkable. All localities at the base of the upper Urswick Limestone possess either 8 or 9 cement cycles and the general characteristics of each cycle are similar with respect to thickness, although the relative intensities of luminescence do vary slightly and some very thin cycles are only locally well developed (Fig. 6c). For example, the sequence at Stainton Quarry (Fig. 5a) is almost identical to those at Warton Crag (Fig. 5d) and Trowbarrow Quarry (Fig. 5c), overgrowths from Holme Park (Fig. 7a) and Jack Scout Cove (Fig. 6c, d) differing only slightly in detail.

Morphologically similar contouring cements from the late Dinantian of Derbyshire have dissolutional breaks at a similar position (Walkden and Berry, 1984b). Another good example with dissolutional breaks is figured by Solomon (1989) from the late Dinantian of North Wales (his fig. 12). However, the precise zonal pattern appears to vary between platforms such that interplatform correlation is not feasible. Calcite cements in which growth was interrupted by events that caused the development of more crystal facies, rather than by simplification and reduction in the numbers of facies, were first noted by Braithwaite and Heath (1989).

Platform margin overgrowths

In four quarries southeast of Carnforth (Fig. 3), where platform margin facies are exposed, a similar phase of syntaxial overgrowth cementation occurs (Fig. 5b). Cement cycle patterns in this setting are more complex than in the platform deposits. This makes correlation difficult, both within a single locality and between platform margin localities, although it is possible to recognise cement cycle sequences in individual localities sampling at 1–2 m vertical intervals. A tentative correlation with the cement cycles in the platform deposits has also been made (Fig. 12). Cement cycles 1 to 3 can be matched with reasonable confidence, but cycles 4 to 8 split into numerous minor sub-cycles in the platform margin area, especially in the upper part of the sequence and cannot be correlated with confidence. In addition extra cement cycles, unique to the platform edge, also occur after cement cycle 8.

Comparison with overgrowths from Asbian limestones in Derbyshire

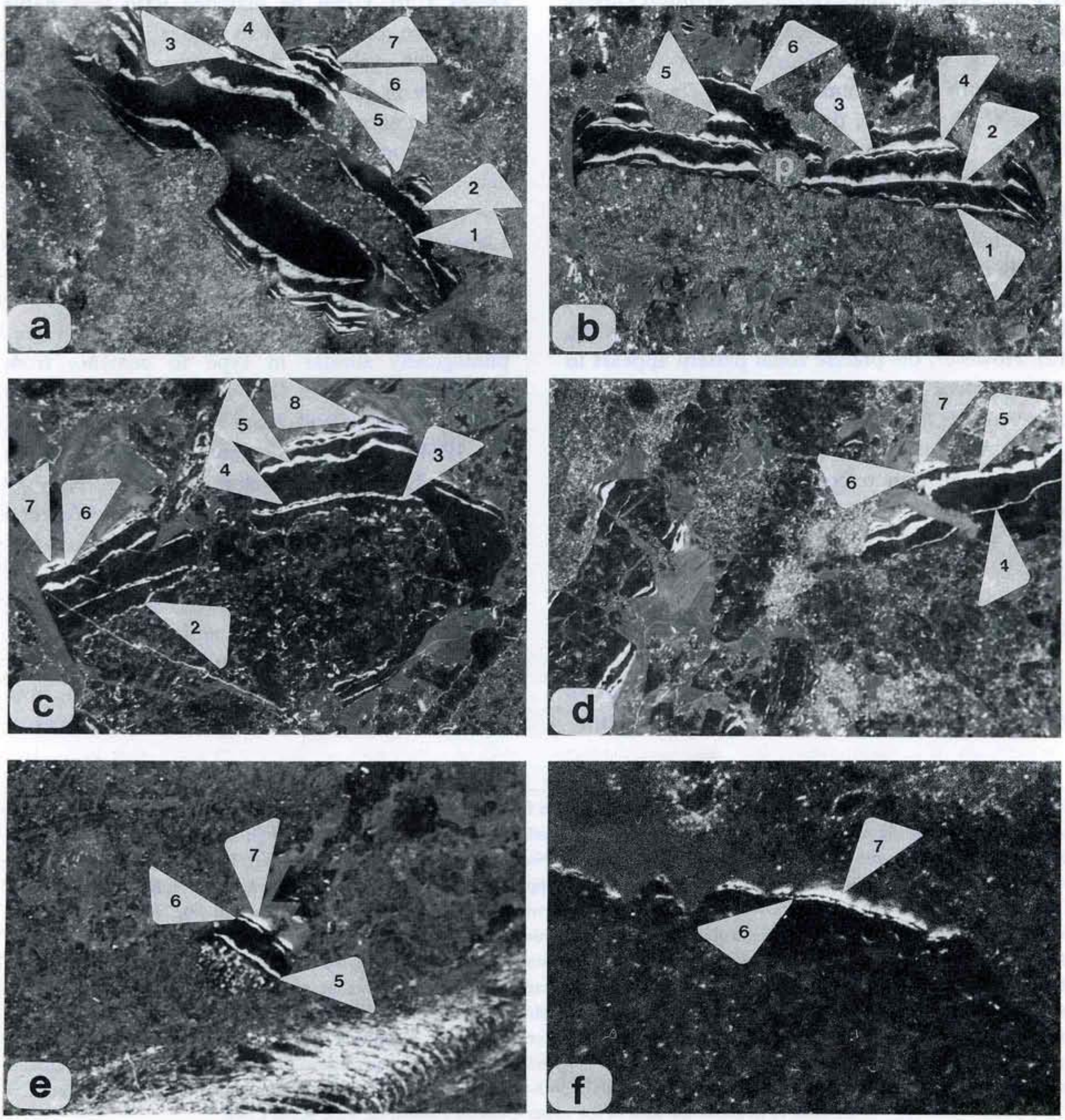
The zoned overgrowths described here are morphologically similar in type to cements from Asbian limestones in Derbyshire figured in Berry (1984), Walkden and Berry (1984a, their figs. 2b, 4a; 1984b, their figs. 2c and 3a) and Walkden (1987). These also develop in an increasingly euhedral form, which was suggested by Walkden and Berry (1984b) to be the consequence of repeated dissolution–precipitation cycles on an originally stabilised but irregularly shaped nucleus, the alternating luminescent and non-luminescent zonation defining growth "pseudofaces".

The Derbyshire overgrowths also occur in a cyclic platform sequence isolated from sources of

Fig. 6. (a) Cathodoluminescence view of the same overgrowth as in Fig. 5c and neighbouring crystals. These demonstrate similar zone sequences, although the basal luminescent zone is not always developed. The overgrowth indicated on the right (*i*) has an irregular development of zones, probably reflecting the plane of section. Note the increasingly euhedral habit of most overgrowths, and the later brown luminescent burial cements. Most of the nuclei are supported by other grains. Cathodoluminescence, field of view 4 mm, 10 m above the base of the upper Urswick Limestone, Trowbarrow Quarry. (b) Plane polarised view of (a). Note the grainstone texture, abundance of tubular *Kamaenella* nuclei (*k*), and the echinoderm spines (*e*). From the calcite cleavages it can be seen that the maximum growth of these overgrowths was parallel to the *c*-axis. Details as above. (c), (d) Overgrowth sequence from Jack Scout, demonstrating that zones are not equally well developed in all examples. Fig. 6c contains an initial twin luminescent zone (1a, 1b), whilst (d) reveals a good outer sequence of cement cycles, euhedral subzones indicating crystal growth forms within zone 2 and possible dissolutional or growth hiati at the base of luminescent zones (arrowed). There is a change in growth form from an initially spired to a later euhedral form within a cement cycle, this is apparent in cycles 1b and 2. Also note how the cements grew around allochems rather than displacing them, this suggests a simple pore-filling type of cementation. Cathodoluminescence, fields of view 0.5 mm, 12 m above the base of the upper Urswick Limestone, Jack Scout Cove.

laterally fed groundwaters (Fig. 1), similar to the geological setting proposed for the Urswick Limestone. However, there are a number of important differences as outlined below:

(1) The overgrowths described by Walkden and Berry (1984a) occur in packstones and wackestones. Those described here occur in depositional grainstones, although as noted by Horbury (1987) many of these appear as "packstone" and "wackestone" textures since they are compacted peloidal grainstones in which most early diagenetic cements are absent. It is in these compacted peloidal grainstones that the overgrowths are often best developed (Fig. 5b), i.e. where earlier diagenetic phases are poorly developed and which would have possessed high original permeabilities.



Suitable unmicritised substrates are present in true packstones and wackestones of the Urswick Limestone but did not develop overgrowths due to either, or both, lack of space in which to grow, or because low permeabilities prevented significant movement of precipitating fluids through the limestone. The depositional grainstones can easily be distinguished from depositional packstones and wackestones on the basis of allochem assemblages, by the presence of detrital clay minerals and fine calcite spar in burrows (Horbury, 1989).

(2) Walkden and Berry (1984a) attributed the Derbyshire overgrowths to cement precipitation in pores created by the solution of metastable micritic sediment ("solution coronas") by Mg-rich fluids in the vicinity of crinoid ossicles undergoing stabilisation. As explained earlier, it is considered that lime mud at a given horizon in the Urswick Limestone had stabilised well before development of such overgrowths at a given horizon. The overgrowths described here grew solely into primary intergranular porosity, which was limited mostly to grainstones. Echinoderm fragments were stabilised during early diagenesis and then acted as nuclei for cements ranging from marine to shallow meteoric in origin, prior to development of the zoned cements.

(3) Walkden and Berry (1984a) record similar cement sequences in non-overgrowth cements. These correlatable cements in the Urswick Limestone are restricted to syntaxial overgrowths on large, monocrystalline substrates and only very rarely did equivalent simple pore-fill cements develop, however large the crystal sizes. Earlier (shallow meteoric) and later (burial) cements may be often developed as both overgrowths and as simple pore-fills nucleated on multicrystalline substrates. The distinction between types of zoned luminescent/non-luminescent cements was not made by Walkden and Berry (1984a) but, in the case of the Urswick Limestone, recognition of the variety of cement types is of fundamental importance. This has permitted accurate determination of the distribution and, therefore, the controls on precipitation of all these cement types. If observed in the Urswick Limestone we would not consider the cements in their figs. 6a and 6b (1984a) to be of the same generation or origin as the correlatable overgrowths in nearby pore-fills.

(4) Berry (1984) and Walkden (1987) describe a cement distribution in which individual luminescent zones, although sometimes traceable laterally within a single depositional sedimentary cycle for more than 10 km, persist vertically for only a few tens of metres. Each zone has an overlapping, but slightly higher stratigraphic range than the previous zone (Walkden, 1987, fig. 8.6). New luminescent zones appear successively to replace earlier zones as they disappear (Fig. 9b). In the Urswick Limestone one cement cycle may be present through more than 90 m and although first formed cement cycles disappear, no new ce-

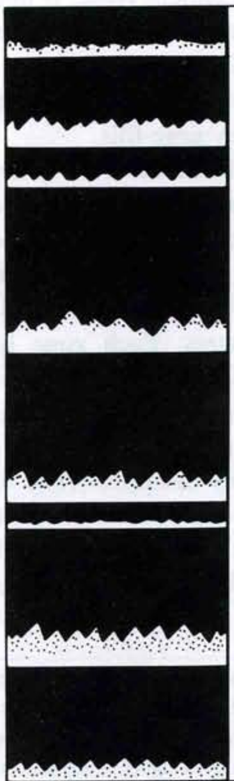
Fig. 7. (a) Platform-type syntaxial overgrowth sequence typical of Holme Park Quarry. This sequence shows the most variation from the typical platform sequence, with some differences in zone character. The first two luminescent zones (1 and 2) are orange luminescent, as elsewhere, but the third and fourth zones are much more closely spaced than those elsewhere and almost appear as one zone with a dull partition. The fifth luminescent zone occurs very close to the fourth and the sixth to eighth zones are similar in development to those elsewhere. Cathodoluminescence, field of view 1 mm, Holme Park Quarry. (b) Syntaxial overgrowth from immediately beneath the upper limit of cement cycle 1 development at Trowbarrow Quarry. Note the great similarity with the cyclicty shown in Fig. 5c, a sample from 10 m beneath. Cycles 7 to 8 are absent in this example. The presence of a peloid (*p*) in the centre of the overgrowth has led to the propagation of growth defects as the cement grew around this obstruction. Cathodoluminescence, field of view 1 mm, 19 m above the base of the upper Urswick Limestone, Trowbarrow Quarry. (c) In this example from 40 m above the base of the upper Urswick Limestone at Trowbarrow Quarry the basal cement cycle (no. 1) is absent. Cycles 2 to 7 are present. Cathodoluminescence, field of view 1 mm, Trowbarrow Quarry. (d) Only cement cycles 4 to 7 are present in these overgrowths 60 m above the base of the upper Urswick Limestone at Trowbarrow Quarry. From this stratigraphic level and above the overgrowths are poorly developed. Cathodoluminescence, field of view 1 mm, Trowbarrow Quarry. (e) Cement cycles 5, 6 and 7 in an overgrowth 75 m above the base of the upper Urswick Limestone at Trowbarrow Quarry. Cathodoluminescence, field of view 1 mm, Trowbarrow Quarry. (f) Overgrowth from 75 m above the base of the upper Urswick Limestone at Trowbarrow Quarry in which only the outer two cement cycles 6 and 7 are developed. Note the progressive loss of cement cycles in the sequence that runs from Figs. 5c, 7b-f. Documentation of the progressive loss of basal cement cycles allows these overgrowths to be used as stratigraphic markers on this platform. Cathodoluminescence, field of view 0.5 mm, Trowbarrow Quarry.

ment cycles appear to replace them (Figs. 9a, 13). The shallow meteoric overgrowth cements (Fig. 4d), discussed earlier, are restricted principally to the lower Urswick Limestone and are not genetically related to the cements discussed in this paper. If these are included in a summary of cement distribution, then a similar pattern emerges to that for Derbyshire. Careful distinction between cement types is, therefore, necessary for the correct interpretation of both generations.

Discussion

Controls on luminescence intensity

Many workers have discussed the factors which influence the colour and intensity of visible luminescence from carbonate minerals, (e.g. Carpenter and Oglesby, 1976; Fairchild, 1983; Machel, 1985; Ten Have and Heijnen, 1985; Hemming et al., 1989). Variations of luminescence in diagenetic calcites have usually been found to be



Cement cycle	Thin orange	Thick orange	Thin yellow then thick orange	Thick yellow then thin orange	Thick yellow	Thin yellow	Thin yellow then thin orange	Thin orange then thick yellow	General character of cement cycles
Σ =	29	11	8	62	117	90	8	3	
8	6	0	0	7	5	8	2	0	Thin to absent cycle. Thick to thin orange or yellow cycle base.
7	2	2	0	14	22	14	1	1	Thin — thick cycle. Thick yellow cycle base.
6	2	0	0	1	27	25	0	0	Thin cycle. Thick — thin yellow cycle base.
5	1	0	0	8	40	6	0	0	Thick cycle. Thick yellow cycle base.
4	5	3	0	10	8	8	3	0	Thick cycle. Thick yellow — orange cycle base
3	0	0	2	3	8	25	0	1	Thin cycle. Thin yellow cycle base.
2	0	6	2	17	7	4	1	0	Thick cycle. Thick yellow to orange cycle base.
1	13	0	4	2	0	0	1	1	Thick cycle. Thin orange cycle base.

Fig. 8. Typical sequence of cement cycles in the Urswick Limestone, summarised graphically (left) and as a table compiled from observation of 56 thin sections from throughout platform centre localities in which overgrowths were developed. From the table a statistical summary of cement cycles character can be defined and, although there is some variation, each cycle has a distinct character. This is important to note since some observations are from near to the base of a cement cycle's stratigraphic range whilst other observations are from the top of a cement cycle's range. An occasional extra thin cycle sometimes occurs in association with cycles 1 and 3/4, these have not been entered into the table. Also, it can be seen that the luminescent parts of cycles are either homogeneous in luminescent colour (76%) or change from yellow to orange (23%) with only 1% changing from orange to yellow. Compare these data with the overgrowth sequences for individual localities in Figs. 5, 6 and 7.

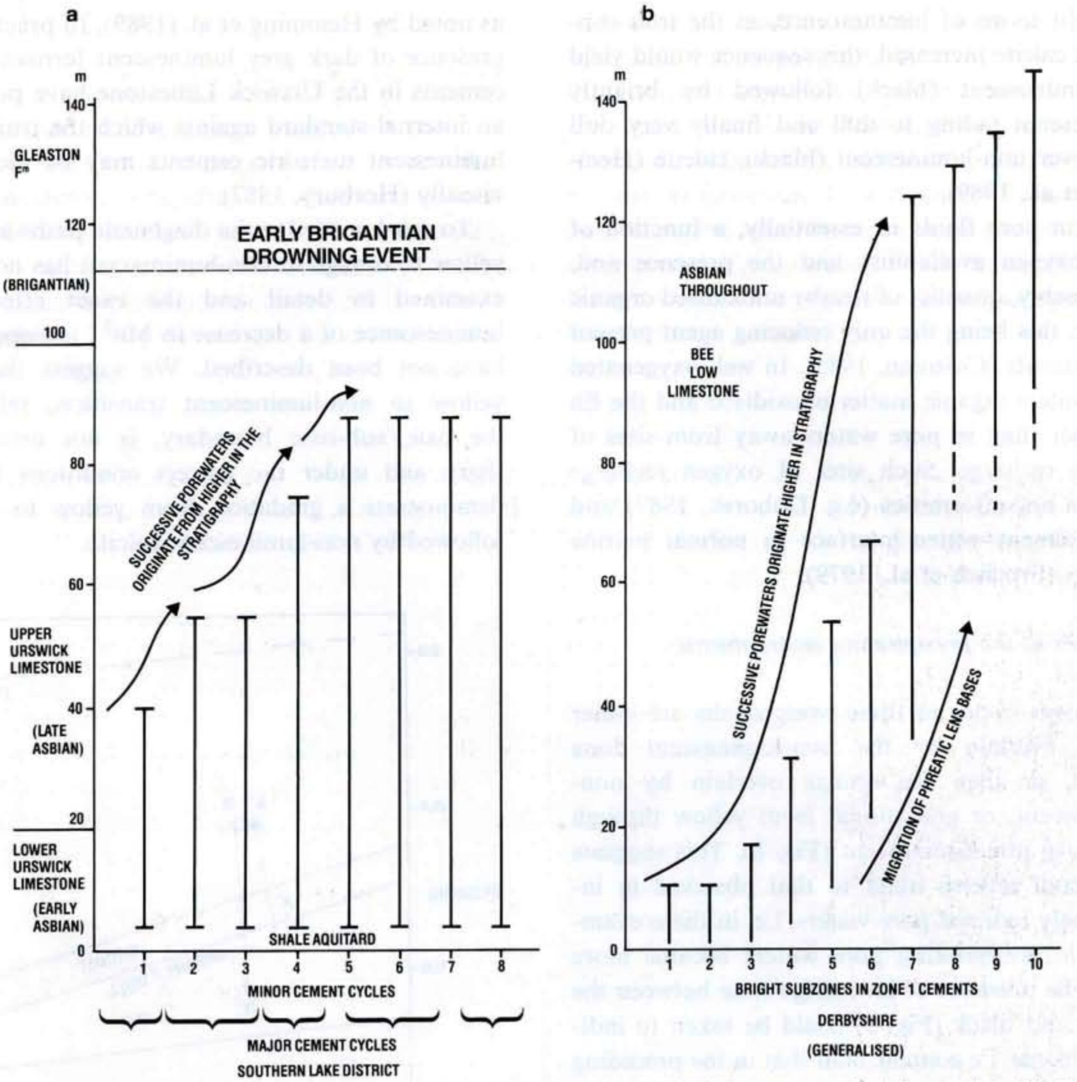


Fig. 9. (a) Graphical summary of cement cycle distributions in the upper Urswick Limestone, revealing the stratigraphically higher upper limit of successive cycles. The cement cycles do not extend below the Woodbine Shale, which is thought to have acted as an aquitard. (b) A summary of the distribution of similar cements from Derbyshire, adapted after Walkden (1987) at the same scale as (a). There are more zones, developed over a thicker section, although individual zones are characteristically more restricted in occurrence. Zone bases move up through the stratigraphy suggesting that there was no Woodbine Shale equivalent to act as an aquitard.

related to changes in the concentration of Mn^{2+} (luminescence activator) and Fe^{2+} (inhibitor) in the calcite lattice, although Machel (1985) stressed the importance of other elements. Incorporation of Mn and Fe into calcite is controlled by the Eh and, to a lesser extent, pH of the precipitating fluid (Garrels and Christ, 1965; Frank et al., 1982). Thus in oxic fluids Mn^{4+} and Fe^{3+} are present and unable to enter the calcite lattice. Reduction of Mn^{4+} to Mn^{2+} occurs in sub-oxic waters and reduction of Fe^{3+} to Fe^{2+} in waters of lower Eh. The reduced forms of Mn and Fe are the only forms that can be incorporated into the calcite crystal lattice. Therefore, in waters in which Eh is decreasing, calcite precipitates will initially lack iron and manganese and will then become more manganoan and finally ferro-manganoan, a sequence predicted by Carpenter and Oglesby (1976). This is the characteristic pathway inferred from most studies of ancient examples (see Introduction). In terms of luminescence, as the iron content in calcite increased, this sequence would yield non-luminescent (black) followed by brightly luminescent fading to dull and finally very dull but never non-luminescent (black), calcite (Hemming et al., 1989).

Eh in pore fluids is, essentially, a function of both oxygen availability and the presence and, presumably, quantity of nearby unoxidised organic matter, this being the only reducing agent present in sediments (Coleman, 1985). In well oxygenated pore waters organic matter is oxidised and the Eh is higher than in pore waters away from sites of oxygen recharge. Such sites of oxygen recharge include unconformities (e.g. Doborek, 1987) and the sediment–water interface in normal marine settings (Froelich et al., 1979).

Eh fields of the precipitating environments

Cement cycles in these overgrowths are either yellow overlain by the non-luminescent zone (black), or they are orange overlain by non-luminescent, or gradational from yellow through orange to non-luminescent (Fig. 8). This suggests an overall reverse trend to that observed in increasingly reduced pore waters, i.e. in these examples the precipitating pore waters became more oxic. The presence of an orange zone between the yellow and black (Fig. 8) could be taken to indicate a higher Fe content than that in the preceding yellow zone, but microprobe and staining data suggest that this change in luminescence colour is not controlled by the presence of Fe^{2+}, but rather by a gradual decline in concentration of Mn^{2+}.

On the basis of visual observations of luminescence it is possible to confuse dark grey and black calcites, this is of importance since they contain different proportions and concentrations of Fe and Mn (Fairchild, 1983; Hemming et al., 1989). They therefore represent different ends of the Eh spectra. Dark grey calcites tend to be ferroan (over 10,000 ppm; Pierson, 1981; Fairchild, 1983) and indicate a low Eh. The absence of significant (> 200 ppm, Machel, 1985) detectable Fe^{2+} in the "non-luminescent" zones present in these overgrowths suggests that these are of the same non-luminescent (black) type (representing a high Eh) as noted by Hemming et al. (1989). In practise the presence of dark grey luminescent ferroan burial cements in the Urswick Limestone have provided an internal standard against which the truly non-luminescent meteoric cements may be identified visually (Horbury, 1987).

To our knowledge the diagenetic pathway from yellow to orange to non-luminescent has not been examined in detail and the exact effects on luminescence of a decrease in Mn^{2+} incorporation have not been described. We suggest that this yellow to non-luminescent transition, reflecting the oxic/sub-oxic boundary, is not necessarily sharp and under the correct conditions it may demonstrate a gradation from yellow to orange followed by non-luminescent calcite.

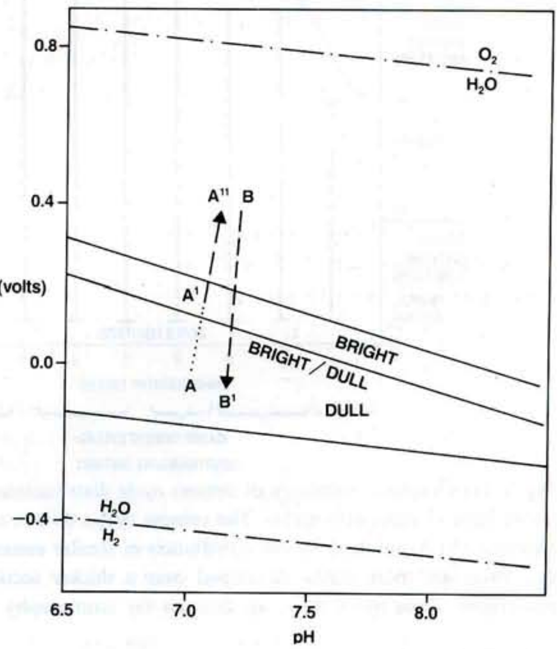


Fig. 10. Modified Eh/pH diagram after Barnaby and Rimstidt (1989). On this the fields of occurrence of varieties of luminescent calcite are plotted, and a typical diagenetic pathway, as inferred by Carpenter and Oglesby (1976) is represented (*B-B'*). This represents the progressive stagnation of a meteoric lens with precipitation of calcite throughout. The line *A-A''* represents the diagenetic pathway inferred for cement cycles in the Urswick Limestone. This in turn represents the establishment of progressively more oxic pore waters, although precipitation is limited to the pathway *A'-A''* because calcite was undersaturated in solution from *A-A'*. Positions of pathways could fall anywhere along the pH axis assuming the Eh is correct since their relationship to pH is uncertain. Their represented positions are for graphical purposes only.

The non-luminescent cements are, therefore, interpreted to have precipitated from oxic pore waters in which Mn^{2+} and Fe^{2+} were absent. Each cement cycle thus represents a precipitate of increasingly oxic pore water, in which precipitation commenced in the sub-oxic zone and the yellow to orange transition reflects a change (probably a decrease) in Mn^2+ concentration during increasing oxidation (Fig. 10). The presence of Mn^{2+} and the absence of Fe^{2+}, within the detection limits of the microprobe, suggests that the calcite is likely to be type IV, a Mn-Pb activated type, typical of diagenetic calcites as defined by Machel (1985).

Environment and controls on cyclic precipitation of calcite in the overgrowths

A variety of observations suggest that the cyclicity of these cements is, in some way, related to the periodic re-establishment of relatively shallow (15–120 m) meteoric phreatic water bodies. These are:

(1) the persistence of individual cement cycles through up to 90 m of the Urswick Limestone;

(2) the intimate stratigraphical association of these cements within a cyclic sequence in which emergent surfaces are well developed (also true for morphologically similar Asbian and Brigantian cements in Derbyshire; Walkden, 1987); and

(3) the paragenetic position of these cements, post-dating shallow (< 15 m) meteoric fabrics and pre-dating burial cements.

Trends in Eh derived from interpretation of cement cyclicity suggest that precipitation was limited to the oxic and sub-oxic fields and that pore waters were either never anoxic or precipitation in the anoxic field did not occur. In cyclic depositional environments during and after marine transgression, the marine deep phreatic environments, tens of metres beneath the sea bed, are likely to have been anoxic (e.g. Froelich et al., 1979). The question, therefore, arises as to why there were no precipitates which reflect this anoxic environment.

Pore-water evolution during transgression

The evolution of pore-water chemistry during shallow (< 15 m) burial of carbonates, in a cyclic depositional setting, is likely to have been complex. During marine transgression the shallow (15–120 m) meteoric phreatic pore waters would exchange with marine phreatic pore waters by density inversion, with the meteoric waters rising through the sediment column. This is because, in order to maintain a meteoric aquifer in a mixed meteoric/marine setting, both a hydrostatic head and/or lateral flow is needed in the meteoric aquifer (Upson, 1966). During transgression both the hydrostatic head and circulation of the meteoric water would have been lost, resulting in disequilibrium of the meteoric aquifer. It is likely that a mixing zone would develop at both the sediment–water interface and at the basal contact of the meteoric lens, with marine waters moving in at depth. Marine deep phreatic pore-water systems are not subject to the very active current, tidal and wave driven water pumping process as associated with near sediment surface marine cementation (Longman, 1980). Also, as noted by Longman (1980), although pore-water movement is possible in the "stagnant" marine phreatic diagenetic environment, the lack of cementation in this setting probably reflects the absence of other factors such as CO_2 degassing and organic activity. It is likely that the marine deep phreatic diagenetic environment in the Urswick Limestone was also one of non-precipitation and perhaps slight dissolution.

The mixing zone is rarely a site of calcite cementation except towards the ends of the mixing spectrum (e.g. Ward and Halley, 1985). Dissolution is more typical of the mixing zone, particularly in the centre of the mixing spectrum. The geological setting of Ward and Halley's (1985) work, a Pleistocene mixing zone in the Yucatan Peninsula, Mexico, closely resembles that suggested for the Urswick Limestone and forms a useful analogue. In their example a 70 m thick meteoric groundwater lens presently floats on marine composition saline brines. Emergence of the normal marine Yucatan carbonate platform was controlled by glacio-eustacy. During regression mixing zones were initially sites of calcite dissolution but as the meteoric water content increased, high-Mg, then low-Mg, calcites may precipitate. Mixing-zone dolomites only occur close to the platform margin, where the mixing zone could be maintained in one place for long periods. A zone of dolomitisation of age equivalence to the correlatable zoned overgrowths occurs immediately above the Woodbine Shale, this may represent a similar resting place of the mixing zone during emergence (Horbury, 1987). Therefore, by analogy, the non-meteoric shallow (15–120 m) burial early diagenetic history of the Urswick Limestone platform centre is likely to be one of non-precipitation to dissolution. In this respect the Urswick Limestone would also be similar to most other shallow marine carbonates.

Pore-water evolution during regression

During relative sea-level fall (regression), providing exposure occurred, meteoric waters would have become established immediately below the emergent surface and these would have displaced the marine waters beneath until limited by hydrostatic head pressure, water circulation patterns (e.g. Upson, 1966) or by an aquitard. It is likely that a mixing zone directly analogous to the Yucatan example described by Ward and Halley (1985) would have been present. As noted previously mixing zones are often sites of dissolution of calcite and aragonite. In a shallow mixing zone developed during regression, the pore-water Eh is likely to be influenced by decay of marine organic material recently incorporated into the sediment, by oxygenated surface water and, to a minor degree in the Dinantian, surface-derived organic material. Such a mixing zone would probably have been anoxic to suboxic, also suggested by the precipitation of yellow luminescent calcite in the most meteoric parts of Yucatan mixing zones during the Pleistocene (Ward and Halley, 1985).

Above the mixing zone were more fully oxygenated meteoric waters. These are likely to have been marginally saturated to oversaturated with respect to calcite, since there would be a considerable supply of carbonate present in freshly deposited sediment which would be metastable in a meteoric setting. Most meteoric precipitation in the Urswick Limestone is known to have been in the vadose and shallowest (< 15 m) phreatic zones (Horbury, 1987). It is in these shallow meteoric waters that freshly deposited aragonite and high-Mg calcite either dissolved or stabilised by neomorphism, whilst precipitation of meteoric cements was at a maxima, as suggested by their volumetric abundance (Horbury, 1987). Compositions of the meteoric waters which penetrated deeper (below 15 m) were only marginally saturated with respect to calcite since the "excess" calcium carbonate had probably been precipitated higher in the section. This is reflected by the low volume of cement precipitated as correlatable overgrowths and in turn suggests that there were no locally available sources of metastable calcium carbonate.

We propose that the only early diagenetic environment in which calcite precipitated beneath the shallowest (< 15 m) meteoric zone was the shallow (> 15 m) meteoric phreatic zone and part of the underlying mixing zone into which the meteoric waters graded, as the mixing-zone waters were flushed away. These precipitating environments would probably have been initially slightly suboxic, reflecting the "tail" of the mixing zone, with later waters being fully oxic. This model of Eh evolution and precipitation matches that interpreted from CL patterns in each cement cycle. Other observations supporting this model are that the overgrowths demonstrate dissolutional hiati prior to precipitation of yellow luminescent calcite (a mixing-zone effect, also observed in the Pleistocene examples of Ward and Halley, 1985). Also, correlatable zoned overgrowths only developed on large nuclei. This suggests that a large "seed" was necessary for crystal growth via competitive crystallisation (Bathurst, 1975). Competitive crystallisation, in which equivalent pore-fill cements were absent, reflects phreatic diagenetic environments which were only marginally capable of precipitating calcite due to minimal pore-water movement and pore waters just saturated with respect to calcite, as proposed by Longman (1980) for the stagnant meteoric phreatic environment.

By analogy with Upson's (1966) work on shallow burial coastal aquifers of the east coast of the U.S.A., establishment of meteoric lenses and their equilibration with marine aquifers, in a glacio-eustatically influenced sequence, should have been relatively rapid. It is unlikely that "trapped" meteoric lenses existed.

The development of additional crystal faces during cement cycle initiation may reflect poisoning of growth by organics and/or trace elements at many points on the overgrowth surface, as suggested by Braithwaite and Heath (1989) for similarly complex overgrowths. Such poisoning may be most likely during earliest meteoric diagenesis before a geochemically homogenous meteoric lens was established.

Model for the precipitation of cement cycles

We suggest a model (Figs. 10, 11a) for precipitation of cement cycles in shallow (15–120 m) burial diagenetic environment as follows:

(1) Marine phreatic diagenesis. No precipitation, perhaps minor dissolution; Mn and Fe both in 2+ valency state.

(2) Early mixing-zone diagenesis. A mixing zone migrated down through the sequence following marine regression and development of an emergent surface. The mixing zone was probably undersaturated with respect to calcite and Eh was slightly more positive than that of the marine phreatic water body. Mn and possibly Fe would be in a 2+ valency state.

(3) Initial meteoric phreatic/late mixing-zone diagenesis. In this interval the pore waters were marginally saturated with respect to calcium and precipitated calcite only on large, monocrystalline nuclei. The Eh would have been sub-oxic, reflecting the influence of the tail end of the mixing zone, with only Mn in the 2+ valency state. Calcites in this diagenetic environment are manganoan and their luminescence was yellow to orange. They only precipitated on certain points of the underlying non-luminescent substrate, probably because of surface poisoning by trace elements and organics.

(4) Later meteoric phreatic diagenesis. A gradual increase in the pO_2 and, therefore, Eh of pore waters as the residue of the mixing zone was flushed away, resulted in precipitation of non-luminescent (black) calcite. The transition from (3) to (4) is reflected by a change in luminescent colours perhaps also as a consequence of declining availability of Mn^{2+}, or by an increase in rate of precipitation of calcite, diluting the manganese content (G. Walkden, personal communication, 1988).

(5) Re-establishment of a mixing zone and marine phreatic diagenetic environment during which time precipitation ceased and minor dissolution may have occurred.

This model is at variance with that of Walkden and Berry (1984a) and Walkden (1987) who interpreted the brightly luminescent intervals as representing marine transgressions, rather than regressions (Fig. 11b). We suggest that during marine transgression the diagenetic environments established would not have precipitated any cements (Fig. 11a).

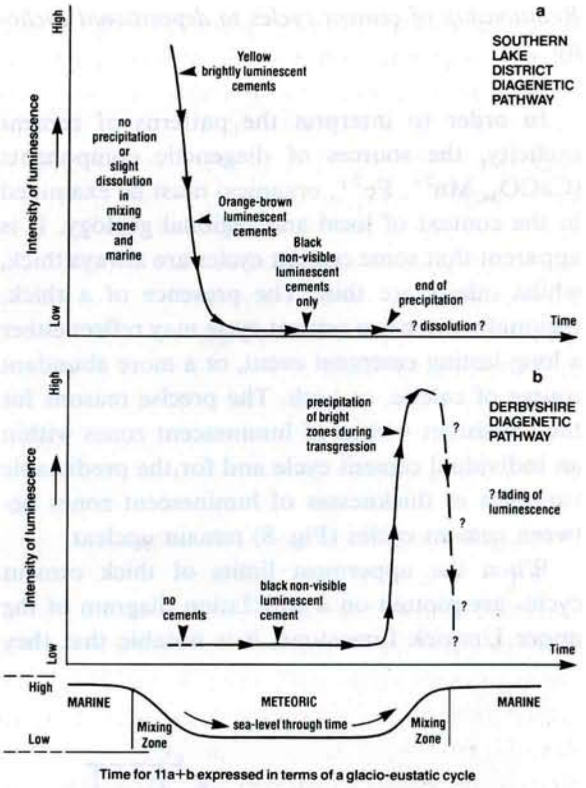


Fig. 11. (a) Model for the precipitation of individual cement cycles as inferred for the Urswick Limestone. Precipitation of yellow luminescent calcite commenced in the latest mixing zone water. This was followed by precipitation of orange and then non-luminescent calcite which continued through emergence until transgression of marine waters led to stagnation and non-precipitation. (b) Interpretation for similar cements for Derbyshire, after Walkden (1987). This model is obviously different, with bright luminescent cements being precipitated during marine transgression.

Relationship of cement cycles to depositional cyclicity

In order to interpret the patterns of cement cyclicity, the sources of diagenetic components ($CaCO_3$, Mn^{2+}, Fe^{2+}, organics) must be examined in the context of local and regional geology. It is apparent that some cement cycles are always thick, whilst others are thin. The presence of a thick, regionally extensive cement cycle may reflect either a long-lasting emergent event, or a more abundant source of calcite, or both. The precise reasons for the consistent widths of luminescent zones within an individual cement cycle and for the predictable variation in thicknesses of luminescent zones between cement cycles (Fig. 8) remain unclear.

When the uppermost limits of thick cement cycles are plotted on a correlation diagram of the upper Urswick Limestone, it is notable that they usually fall beneath depositional cycle boundaries (Fig. 12). Moreover, successive thick cement cycles occur beneath successively higher depositional cycle boundaries. Therefore, it appears that some factor associated with depositional cycle boundaries controlled the development of thick cement cycles. There are two suggested mechanisms:

(1) Firstly, the pore waters that precipitated a thick cement cycle found beneath a given depositional cycle base may have been sourced from one of the emergent surfaces found just beneath that depositional cycle base. Water bodies would, therefore, have been precipitating cements from about 1 to 90 m beneath the emergent surfaces. However, it is difficult to reconcile this model with earlier observations and conclusions. These are that the cements are interpreted as precipitates of the stagnant meteoric phreatic zone which is

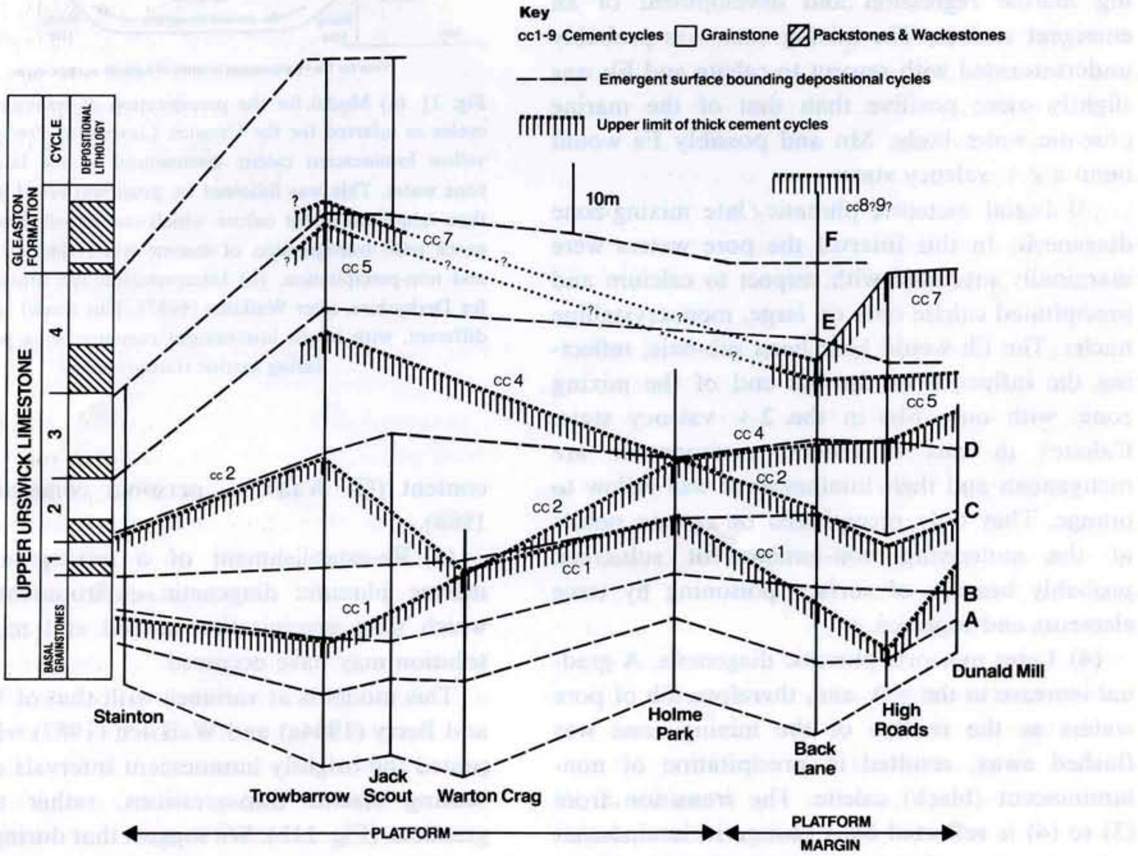


Fig. 12. Representation of upper limits of thick cement cycles from the platform and equivalent platform margin sequences. Data coverage is good for Stainton, Trowbarrow, Holme Park, Back Lane, High Roads and Dunald Mill Quarries. The maximum upper limits of thick cement cycles are usually just beneath the development of thick depositional cycle packstones and wackestones.

not often a near-surface diagenetic environment (Longman, 1980). Also, a great variety of earlier meteoric cement fabrics occur at depths of up to 10–15 m beneath emergent surfaces, and do not demonstrate the zonal sequence typical of the correlatable cements. It is difficult to envisage how several fundamentally different cement morphologies, known to be widely separated in the paragenetic sequence, could precipitate separately within the same porespace during the course of a single emergent event, this sequence of events then being predictably repeated during subsequent emergent events. Additionally, emergent surfaces in the lower Urswick Limestone and the lower part of the upper Urswick Limestone are not associated with the appearance of cement cycles, which would be expected if the sole control on cement cycle precipitation was subaerial emergence. This mechanism is therefore discounted.

(2) Secondly, it is suggested that where packstones and wackestones were freshly deposited above the depositional cycle boundary, the subsequent period of emergence would have been responsible for the stabilisation of the constituent lime mud and aragonitic or high-Mg calcite allochems in the packstones and wackestones. It is inferred from this that the packstone–wackestone unit would have had a greater potential to supply carbonate during its initial flushing with meteoric water than during subsequent flushing events. Thick cement cycles may result from carbonate derived from the stabilising of overlying packstones and wackestones. This mechanism is preferred to (1).

Thin cement cycles would reflect the karstification and stabilisation of subsequently deposited grainstone. This facies was probably less effective than the packstones and wackestones as a donor of calcium carbonate since these grainstones comprise comparatively low volumes of metastable carbonate phases. It may be the case, but cannot be demonstrated, that the first formed emergent surface above cycle-base packstones and wackestones was also the longest lasting. When the thicknesses, positions and sequence of cement cycles as fixed by the above method are compared to the positions and sequence of palaeokarsts in the stratigraphy, there is a close correspondence across the > 30 km width of the platform. Each emergent event which caps freshly deposited sediment appears to have been responsible for precipitation of an individual cement cycle (Fig. 13).

The lack of any significant or predictable lateral changes in character of the cement cycles suggests that development of each meteoric water body was very uniform across the whole platform. This reflects the laterally homogenous depositional cyclicity (Horbury, 1989) and a uniform rate of regression, which was controlled by glacio-eustacy (Walkden, 1987; Horbury, 1989). Tectonic generation of emergent surfaces would invariably have involved tilting and consequent on this, variability in facies patterns may cause complex meteoric flow paths to develop, as seen in other examples in which there was significant lateral water movement (e.g. Doborek, 1987). The regularity of cement morphologies, therefore, indirectly supports a non-tectonic origin for the emergent surfaces.

Manganese and iron were probably available from newly deposited argillaceous and organic-rich sediment (e.g. Machel, 1985). Such components probably occurred predominantly within the bioclastic argillaceous packstones and wackestones of cycle bases and palaeosol clays. Hydroxyoxides, hydroxides and oxides on the surfaces of clay minerals are the principal source of these trace elements (Curtis and Coleman, 1986).

Platform margin overgrowths

Syntaxial overgrowths (Fig. 5b) which developed within 5 km of the platform margin, near Carnforth (Fig. 3), become progressively more variable as the margin is approached. They may also possess several generations of "flame structures" as also noted in Ordovician carbonates from Norway (Braithwaite and Heath, 1989). These forms are more complex than the generally euhedral crystals initiated on platform centre overgrowths and indicate that growth was irregular and possibly subject to more, or more pronounced, dissolutional or poisoning events by a non-essential ion (e.g. Briathwaite and Heath, 1989). These overgrowths are considered to reflect greater geochemical or compositional heterogeneity of the meteoric phreatic lens near to the emergent platform margin in the Lancaster Fells Basin. Variations could relate to the presence of depositional and karst topography (Horbury, 1987) which would cause localised lateral flow patterns within the meteoric lens; effects of minor eustatic variations on the shoreline position of the lowstand

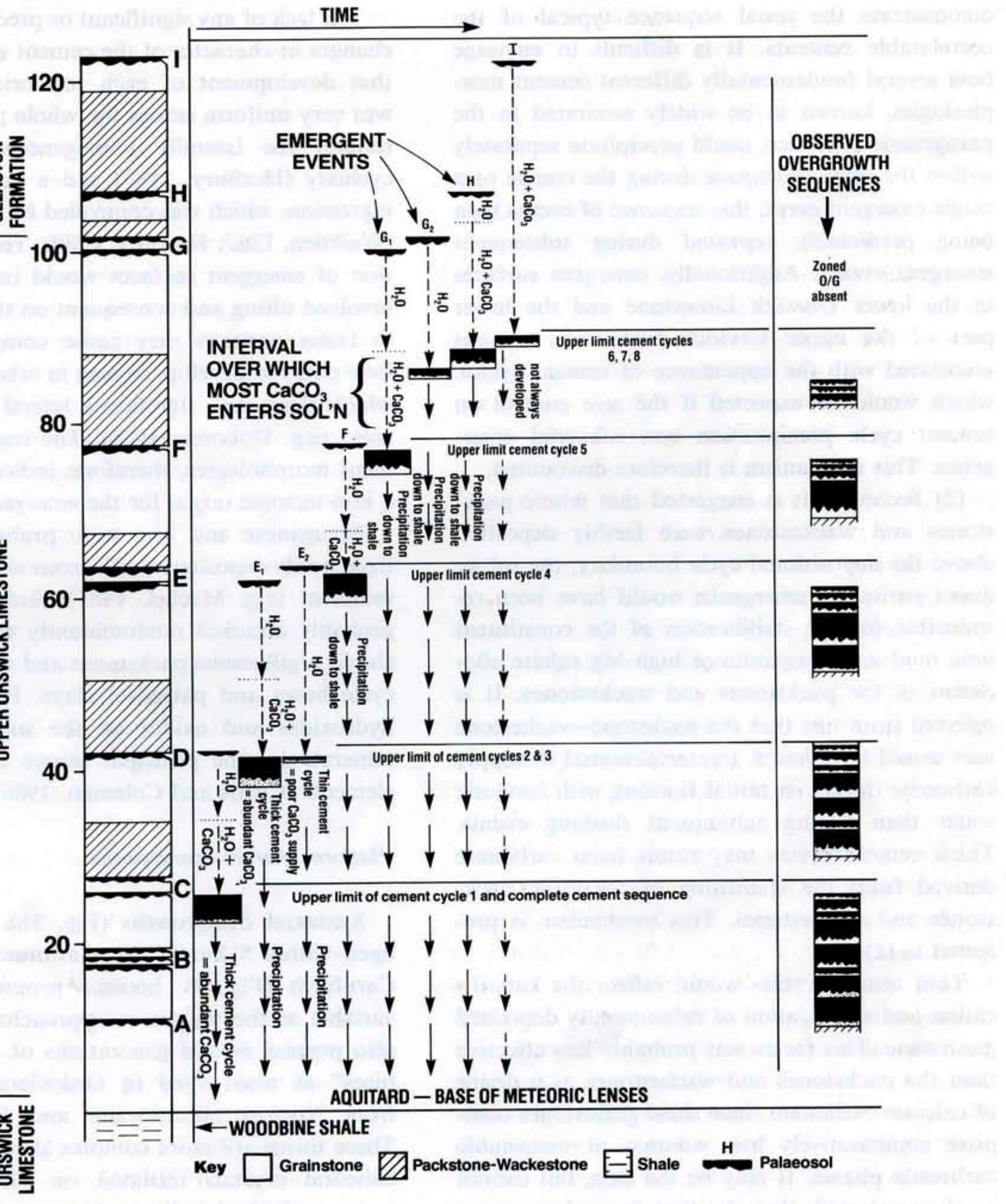


Fig. 13. Model accounting for the relationship between emergent surfaces (as a source of precipitating pore waters), depositional cycle base packstones and wackestones (source of $CaCO_3$ for thick cement cycle development) and the cement cycle sequence itself. The numbers of cement cycles corresponds closely to the numbers of palaeokarsts developed above the upper occurrence of cement cycle 1. A sequence of basinal mudstones developed above emergent surface I and this drowning halted meteoric diagenesis, accounting for the end of precipitation of these types of overgrowth. All the meteoric lenses appear to have extended down to the Woodbine Shale, which probably acted as an aquitard, on which mixing zone dolomites precipitated and beneath which no significant meteoric precipitation occurred during the late Asbian.

sea; affecting hydrostatic head and resulting in marine water incursion or meteoric excursion (e.g. Upson, 1966); localised facies variations resulting in heterogenous poroperm peculiar to the platform margin; and, as suggested by Machel (1985), partitioning of trace elements in coastal meteoric aquifers.

Upper and lower stratigraphic limits

The lower stratigraphic limit of these cements coincides approximately with the top of the Woodbine Shale (Figs. 9a, 13). This suggests that the shale functioned as an aquitard for the meteoric lenses proposed above. In Derbyshire, similar cements are not restricted by an aquitard and are seen to "die out" gradually with depth (Fig. 9b; Walkden, 1987). In the southern Lake District the upper limit for these cements is near to the top of the Urswick Limestone, which, it is proposed, reflects the absence of palaeokarstic surfaces above the basal part of the Gleaston Formation (Fig. 2). The overlying facies are basinal mudstones. It is, therefore, suggested that the cement cycles were precipitated until the carbonate platform was drowned, so that the outer cement cycles are of early Brigantian, rather than late Asbian age. This timing is similar to that of equivalent cements in Derbyshire described by Walkden (1987).

No cement cycles of the type described here appear to be developed in association with the emergent surfaces in the lower Urswick Limestone or the grainstone base of the upper Urswick Limestone. There are several factors which may account for this. In the early Asbian there was nearby emergent land which was being onlapped, this probably contributed meteoric water via lateral flow into the lower Urswick Limestone during both sea-level lowstands and highstands. Such a hydrological regime favoured precipitation of the zoned cements (Fig. 4d) similar in appearance and origin to those described by Meyers (1974, 1978), Grover and Read (1983) and Doborek (1987).

During the late Asbian the whole of Cumbria is thought to have been covered by a flat-topped carbonate platform (Horbury, 1989). In this setting, during both sea-level highstands and lowstands, there were no sources of laterally fed meteoric waters. The palaeokarsts at the base of the upper Urswick Limestone are not obviously associated with the generation of syntaxial overgrowths. This may reflect an originally stable, dominantly non-aragonitic calcite bulk mineralogy of the grainstones which underlie each palaeokarst. These only yielded carbonate for re-precipitation as shallowest meteoric (< 15 m) pore fill cements (Horbury, 1987). The originally porous and permeable grainstones sit above the Woodbine Shale aquitard. During early diagenesis these grainstones probably acted as a shallow meteoric conduit in Longman's (1980) "zone of active water circulation". In this there would have been rapid lateral flow into the lowstand basinal sea, given that the surface of this sea would have been below the level of the shale assuming a > 30 m fall in sea level due to ongoing glacio-eustacy (Horbury, 1989). The presence of the shale aquitard at shallow depth would, in turn, have prevented the establishment of a thick stagnant meteoric lens and thereby prevented correlatable cements from precipitating. This only became possible during burial in the latest part of the Asbian.

Regional controls on similarities and differences of correlatable zoned cement

The intimate relationship of the correlatable zoned cements to a stratigraphy controlled primarily by tectonic response of this platform to extension and with emergence primarily controlled by eustacy (Horbury, 1989) has important regional implications. Firstly, most Asbian platforms in Britain were flat topped such that eustatically controlled emergence resulted in a similar paragenesis for each platform (Walken, 1987). This type of correlatable zoned cement has thus been found on most British Asbian platforms, accepting that differences in interpretation reflect authors' opinions rather than fundamental differences in cement morphology. However, the zone sequence patterns figured for each platform differ significantly in detail, e.g. Derbyshire (Walkden and Berry, 1984a, b), North Wales (Solomon, 1989), South Wales (our presently unpublished observations) and in this paper. We suggest that the inability to match these overgrowth zone sequences between platforms reflects the variability of each platform's subsidence history and hence facies development (e.g. in the importance, frequency and stratigraphic positions of "donor" limestones during the Late Dinantian and also in the precise flow regimes present in each platform).

In summary, the principal ultimate controls on development of correlatable cements on each platform are also the controls on facies architecture of each platform, such that platforms possess diagenetic and depositional similarities due to eustacy and differences due to local tectonics.

Conclusions

(1) Minor cycles of cementation are recognised in syntaxial overgrowths in the upper Urswick Limestone using cathodoluminescence. They consist of multi-faceted, thin, sharply based yellow luminescent, sometimes giving way outwards to, or alternatively being replaced by, orange luminescent and then more simple growth of wide non-luminescent (black) calcite.

(2) Individual cement cycles can be correlated across the platform for at least 30 km and can be traced vertically in stratigraphic sequences for up to 90 m. Cement cycles cannot be correlated between platforms since they represent the interplay of tectonics, eustacy and sedimentation unique to each platform.

(3) The loss of successive basal cement cycles, when traced up through the stratigraphy, and the distinctive appearance of individual cement cycles, enables these cements to be used as platform-wide stratigraphic markers with a resolution better than that provided by microfossils in the same sequence.

(4) These overgrowths occur only in grainstones and did not usually develop in muddy lithologies. They nucleated on echinoderm and other large, monocrystalline calcite substrates, such as the algae *Kamaena* and *Kamaenella*. They only very rarely developed as simple pore-fills, when they precipitated on earlier cements but never on multicrystalline substrates. No evidence has been recorded of solution coronas in wackestones and packstones. The overgrowths differ in these respects from descriptions of the morphologically and temporally equivalent overgrowths described by Berry (1984), Walkden and Berry (1984a, b) and Walkden (1987).

(5) We propose that these calcites were wholly precipitated from relatively stagnant, calcite saturated, shallow (15–120 m) meteoric phreatic and some mixing-zone waters moving downwards from emergent surfaces. Stagnant deep marine phreatic and marine mixing-zone waters slightly undersaturated with respect to calcite were present before and during establishment of each meteoric lens. These were probably responsible for hiati within the crystals.

(6) Zonation reflects the progressive establishment of oxic pore waters after an initial sub-oxic phase. Anoxic pore waters were probably present prior to the sub-oxic pore waters, but did not precipitate calcite since they represent undersaturated marine deep phreatic/mixing-zone environments.

(7) Precipitation of calcite and increasing oxidation of pore waters were consistently covariant, such that in these examples, during the establishment of oxic meteoric lenses, ferroan calcites never precipitated. The precipitation field and Eh pathway during establishment of downwards penetrating meteoric lenses is, therefore, quite different to that determined for laterally fed meteoric lenses.

(8) Changes in luminescence from yellow to orange to black zones outwards probably reflects Mn^{2+} concentration control on luminescence in the absence of Fe^{2+}. This is thought to be due to an increase in Eh (related to an increase in pO_2), accompanied by an increase in the rate of calcite precipitation as the mixing-zone waters were replaced by those of purely meteoric origin.

(9) Thicknesses of cement cycles are thought to primarily reflect the availability of metastable carbonate during emergent events. Emergent surfaces, developed above freshly deposited packstones and wackestones, rich in metastable carbonate, were probably the source of meteoric water which precipitated the thickest cement cycles. Emergent surfaces developed above units consisting only of grainstone were probably the source of meteoric water which precipitated thin

cement cycles. Patterns of cement cyclicity are, therefore, thought to reflect depositional cyclicity. Correlation of cement cycles, in turn, reflects the lateral homogeneity of depositional environments and the uniform response of meteoric penetration to eustatic sea-level falls.

(10) The pattern of cementation becomes progressively more complex approaching the platform margin. This probably reflects local influences of lowstand sea-level changes, irregularities in erosional and depositional slopes, lateral components within meteoric flow patterns, rapid lateral facies variations and trace element partitioning near to the margin.

(11) The lower limit of these cements is a shale aquitard which it is believed prevented further penetration of the meteoric lenses.

(12) Precipitation of these cements ceased when the carbonate platform was drowned early during the Brigantian.

(13) Overgrowths showing such a regular and laterally persistent stratigraphic distribution may be taken as an indicator of the influence of regular sea-level fluctuations on cyclic sediments deposited on a platform isolated from laterally-fed meteoric water.

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