LATER QUATERNERY CARBONATE DIAGENESIS IN THE SEVERN ESTUARY LEVELS: SOME INTRODUCTORY EXAMPLES

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Examples are described and briefly interpreted of four styles of carbonate diagenesis which have the potential to affect the preservation of environmental and archaeological evidence in the area. Local calcite cementation prior to the formation of a (?late glacial) head gave rise to irregular finger- to sheet-like bodies in the otherwise unconsolidated Ipswichian shoreface/beach bioclastic sands exposed at Gold Cliff Island. Flushing by meteoric waters under oxic conditions was the likely cause. The roots of early-mid Holocene forest trees that grew on and penetrated the head on the slopes of the Island became encrusted with siderite-calcite, and these minerals were also precipitated as irregular layers. Meteoric waters were again probably responsible, but, in the presence of abundant plant matter, reducing and anoxic (but largely non-sulphidic) conditions prevailed. The modern high salt marshes associated with the Rumney Formation in the Severn Estuary are locally decalcified. At Cake Pill calcite has been precipitated within the silts of the formation under oxic conditions as a number of horizons of calcite poupées*. As exemplified by exposures at Awre, calcite concretions can also be found in saltmarsh silts of mid Holocene age. Decalcified silts of this date are known locally, but the timing of decalcification and concretion-formation in their case is unknown, but could be penecontemporaneous, like the occurrence at Cake Pill.*

INTRODUCTION

MANY CHANCE FINDS, planned surveys and excavations have amply demonstrated the archaeological richness of the Severn Estuary Levels, where sites and artefacts occur in the context of a very varied sequence of later Quaternary deposits formed during changes in climate and sea-level within the geologically dynamic area of the inner Bristol Channel and Severn Estuary. Crucial to an understanding of the archaeology is an appreciation of the geological factors that determined the changing character of this context. Those factors that controlled the deposition of the sequence are now fairly well understood. Much less is known of those that operated post-depositionally, for example, the slow conversion of green plant material to the peat beds now seen, the pyritisation of organic material, and the occurrence of carbonate diagenesis. The processes responsible for the latter, although thought to operate only locally and perhaps to reflect unusual geochemical conditions, have the ability to change the volume of a body of sediment and its strength in response to compaction and erosion and, together with others, to affect the preservation of materials of archaeological and environmental interest. The following note introduces examples of four different expressions of carbonate diagenesis to be found in the later Quaternary sequence of the Severn Estuary Levels.

DEVENSIAN (GOLD CLIFF ISLAND)

During the Ipswichian (last interglacial) marine high-stand, the margins of the inner Bristol Channel and outer Severn Estuary were shaped into rock platforms and spreads of raised shoreface and beach deposits (Allen 2002). The most impressive example of these surrounds the now much-diminished bedrock island at Gold Cliff (British National Grid ST 3781) on the Welsh coast (Figure 1). The island became surrounded by an accumulation of wave-affected rubble overlain by shelly, calcareous sands, of undoubted Ispwichian age (Haslett 1997, Allen

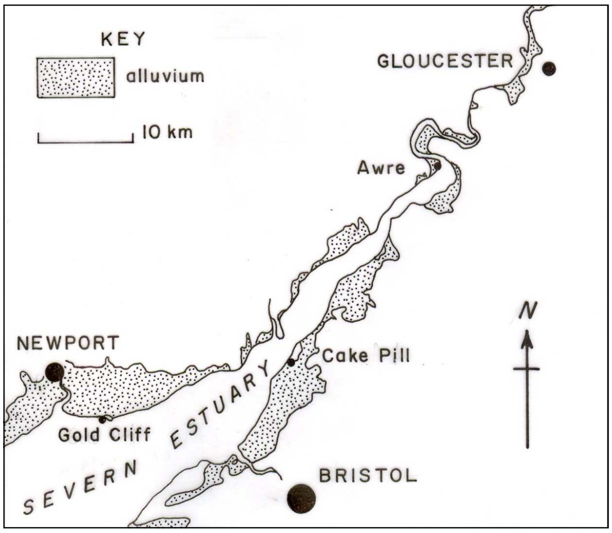

Figure 1. The Severn Estuary Levels, showing places mentioned in the text.

2000), thickest on the sheltered north-eastern side. Overlying these beach and shoreface deposits is a variable development of sandy head, considered to be late glacial in date, derived largely from the Triassic and earliest Jurassic beds that form the island.

The sands within the sequence display varying degrees of calcite cementation (Allen 2000). In places they are uncemented and free-running, in others weak sand-rocks, and in others again in the form of hard, fully-indurated, bedding-parallel finger-like bodies and patterned sheets, separated by unconsolidated material (Figure 2). Broken, angular fragments of calcite-cemented sheets and fingers of similar sand are common within the head and clearly antedate its formation. The fact that the head includes these fragments, and is itself sandy, strongly suggests that beach sand was blown inland onto the slopes of the island either during the Ipswichian or at some time in the subsequent Devensian glacial stage. Partial cementation of the blown sand followed at some time before the creation of the head (?late Devensian).

Under the microscope the fully-indurated sands prove to be very fine- to medium-grained. Typically, the detrital component forms half the rock or less, consisting of quartz sand with subordinate rock fragments (chiefly phyllites and schists), feldspars, well-rounded bioclastic debris (chiefly molluscan fragments, some foraminifera), occasional flakes of mica and chlorite, and scattered well-rounded grains of bright-green glauconite. The occasional granule/small pebble of earliest Jurassic cementstone is occasionally seen. The detrital heavy minerals present, previously reported (Allen 2000), indicate that the sediment was ultimately derived from a largely metamorphic terrain and was probably introduced glacially into the Bristol Channel and Celtic Sea to the west. The presence of a little glauconite, however, perhaps suggests a small contribution from Wessex to the east. Binding the detrital components is a continuous cement of calcite ($CaCO_3$), varying from micrite in the finer-grained sands to a mixture of micrite and microspar or microspar alone in the coarser ones. In some of the thin-sections examined, many quartz grains have ragged, corroded margins, suggesting a degree of replacement by the calcite. The general dominance of micrite-microspar, however, points to a mainly displacive introduction of carbonate, locally increasing the volume of the deposit.

The cemented forms hosted by the Ipswichian sands at Gold Cliff Island exemplify a type of concretionary development common in later Quaternary, especially late glacial, sandy deposits in Britain. They can be found, for example, in the Ipswichian Burtle Beds of Somerset, a series of shelly sands of estuarine-beach origin (Kidston *et al.* 1978), and in much glaciofluvial outwash (eg Allen 1982, Knight 1998). It is generally considered that the dissolved carbonate became available through decalcification by meteoric waters under late glacial and early Holocene vegetation communities. The sources of carbonate are various. At Gold Cliff Island, and also in the case of the Burtle Beds, carbonate is likely to have been provided by the bioclastic element in the sands themselves, if not also through groundwater by the associated Carboniferous and early Jurassic sediments. A groundwater supply is likely in the case of many glaciofluvial outwash deposits.

EARLY HOLOCENE (GOLD CLIFF ISLAND)

The sloping flanks of the island at Gold Cliff are draped by a sequence of Holocene estuarine silts interbedded with peats (Wentlooge Formation) that overlies a palaeosol formed in most places on head but locally on Ipswichian sands (Allen 2000, Bell *et al* 2000, Bell 2007). On this land surface an oak-dominated forest, called the Lower

Figure 2. Gold Cliff Island. Sheet of calcite-cemented Ipswichian shoreface/beach sand exposed on ridge on the north-eastern flank. The linear features are oriented down the gentle dip. Lens cap for scale.

Submerged Forest, began to grow in the sixth/seventh millennium BC, and a similar but more varied forest, the Upper Submerged Forest, appeared in the fifth millennium BC, contributing to the *c* 1 m main peat bed of the area.

The roots of the trees of the Upper Submerged Forest and its upslope extension on the southwestern flanks of Gold Cliff Island in places penetrate down into the head, here a yellow-red, sandy clay to clayey sand with abundant fragments of Triassic mudrock, earliest Jurassic shale and limestone, pieces of Ipswichian cemented sand as described above, and rare mammalian bones and teeth. Associated with the root horizon are two kinds of concretion formed of carbonate minerals. Many of the roots, now represented by voids containing shreds of plant tissue, are encased by stout, tubular, occasionally branching rhizocretions (Figure 3). The largest embraced roots a few centimetres in diameter. The other sort of concretion is irregular and roughly tabular, measuring up to 12 cm in length. These tend to occur along the sandier and more pebbly layers within the head (Figure 4).

In thin-section the concretions display subordinate amounts of the same detrital components as described above from the Ipswichian deposits, with variable amounts of clay minerals in addition. The detrital material in the tabular ones appears to 'float' in a continuous matrix of finely to coarsely granular siderite ($FeCO_3$) set in calcite micrite to microspar with minor amounts of clay minerals, broken only by circular to oval holes with linings and shreds of plant tissue where there were once rootlets. A thin layer of micritic calcite was the first precipitate to form around some root channels. Also 'floating' are the detrital grains in the rhizocretions, but these are set in a dark-brown to black, occasionally reddish, almost opaque groundmass of extremely fine-grained clay and carbonate minerals. X-ray diffraction analysis of 13 representative samples of the two sorts of concretion gave the following compositional ranges: quartz (13.2-48.2%); feldspars (1.4-10.2%); clay minerals (illite, chlorite, kaolinite) (3.9-9.0%); calcite (10.4-63.8%); siderite (19.5-38.7%); haematite (Fe_2O_3) 0.9-4.5%); and pyrite (FeS_2, two samples: 2.4, 2.8%), the only iron

Figure 3. Gold Cliff Island. Selected rhizocretions (tubular concretions), with scale marked in centimetres.

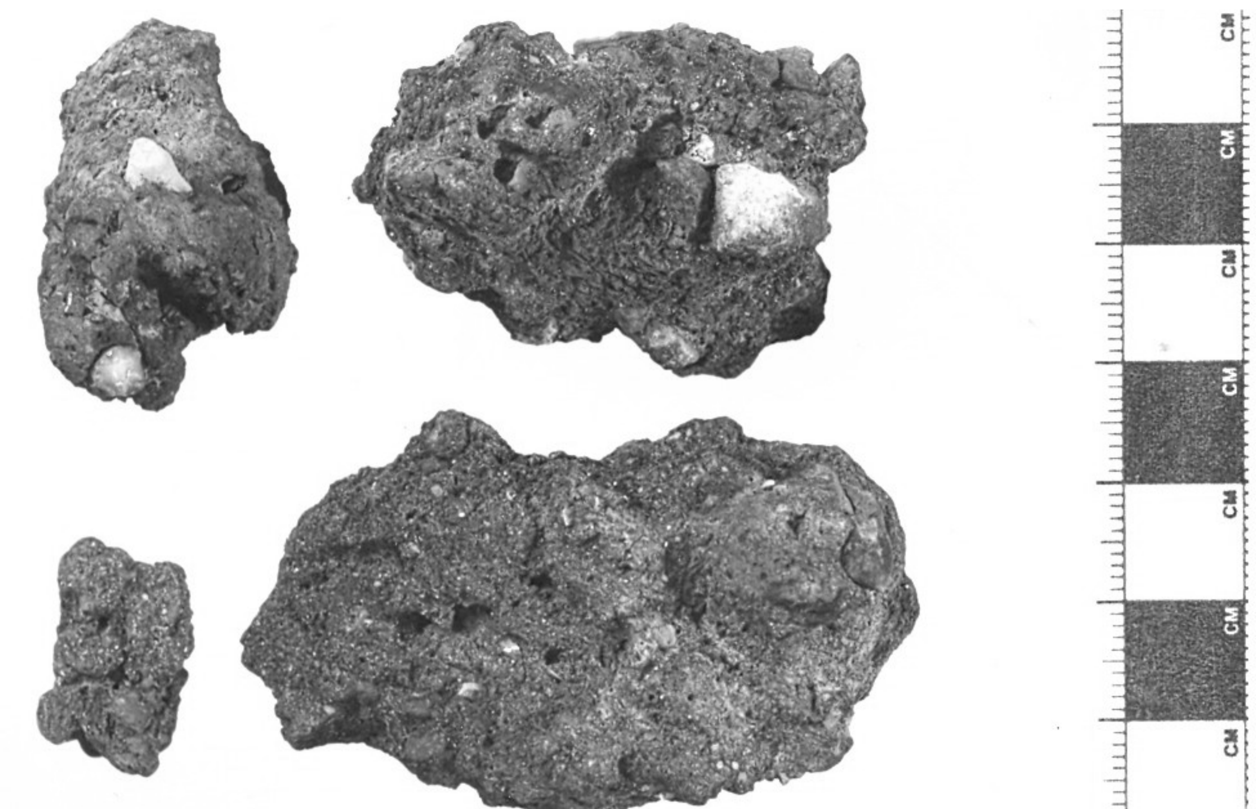

Figure 4. Gold Cliff Island. Selected tabular concretions, with scale marked in centimetres.

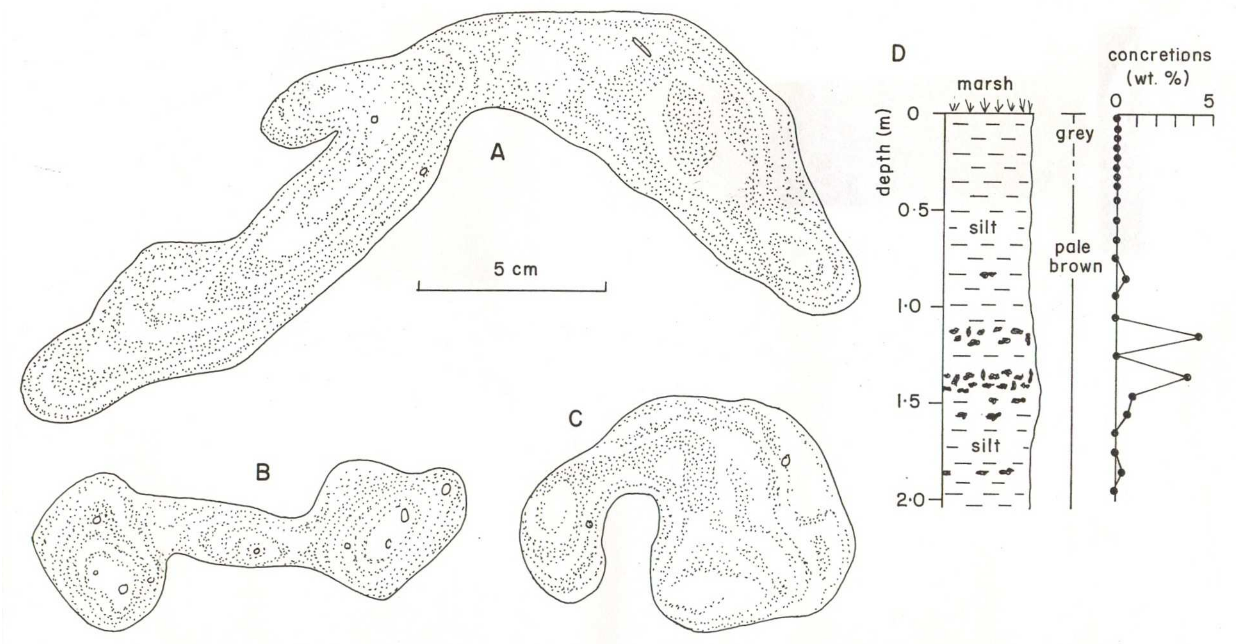

Figure 5. A-C – selected concretions, Awre (NB - some laminae are laterally discontinuous and others cross-cutting). D – profile of the concretion-bearing Rumney Formation, Cake Pill.

sulphide detected. The siderite mineral exhibited minor shifts in peak positions, suggesting that manganese was partially substituted for iron. Chemical analysis by x-ray fluorescence of the same suite of samples revealed 21.4-35.7% of iron (as Fe_2O_3) and 0.60-1.96% of manganese (as MnO). Strontium was present between 167 and 463 ppm, either substituting for calcium in the calcite or in the gypsum (or even as free celestite) occurring in the Triassic sequence.

The mode of occurrence of the siderite links the carbonate diagenesis to the particular geochemical microenvironment associated with the decay of the roots of the trees of the extended Upper Submerged Forest and to the period over which that decay occurred. Authigenic siderite formation is most favoured in organic-rich, reducing, freshwater environments, such as marshes, swamps and lakes (Burdige 1993). Typically, the siderite is not accompanied by iron monosulphides, although a little pyrite (?later) in some cases may also be detected, the diagensis thus falling into Berner's (1981) 'anoxic, non-sulfidic' category. The iron is likely to have been derived from the Triassic rocks mainly underlying Gold Cliff Island, and the setting of the concretions, on its slopes, would have ensured that the meteoric waters probably responsible vigorously flushed the site as they escaped to the surrounding marshes.

Authigenic siderite has previously been reported from other contexts in the Severn Estuary Levels. Siderite microconcretions, some associated with root channels, occur in the Wentlooge Palaeosol immediately underlying the Rumney Formation near Cardiff (Allen 1987). Here, on an eroding coast, wave-action has concentrated these millimetre-scale concretions into localised spreads of sand. From the same area, Mortimer and Rae (2000) reported bands of siderite rhizocretions toward the base of the Wentlooge Formation as well as more widely disseminated microconcretions of the mineral. Kim *et al* (2004), working in the Korean coastal zone, found abundant siderite microconcretions in early Holocene sediments considered to have formed in a swamp or bog a few metres above sea level. These various examples may be contrasted with the style of siderite-authigenesis encountered in saline environments. In the active salt marshes of the north Norfolk coast saline pore fluids held in the sandy silts are subject to strong tidal forcing (Pye *et al* 1990, 1997; Alison and Pye 1994). Here the rapidly-forming concretionary deposits consist chiefly of siderite, iron monosulphides (absent from Gold Cliff Island) and high-magnesian calcite, with some pyrite, exemplifying another of Berner's (1981) anoxic geochemical

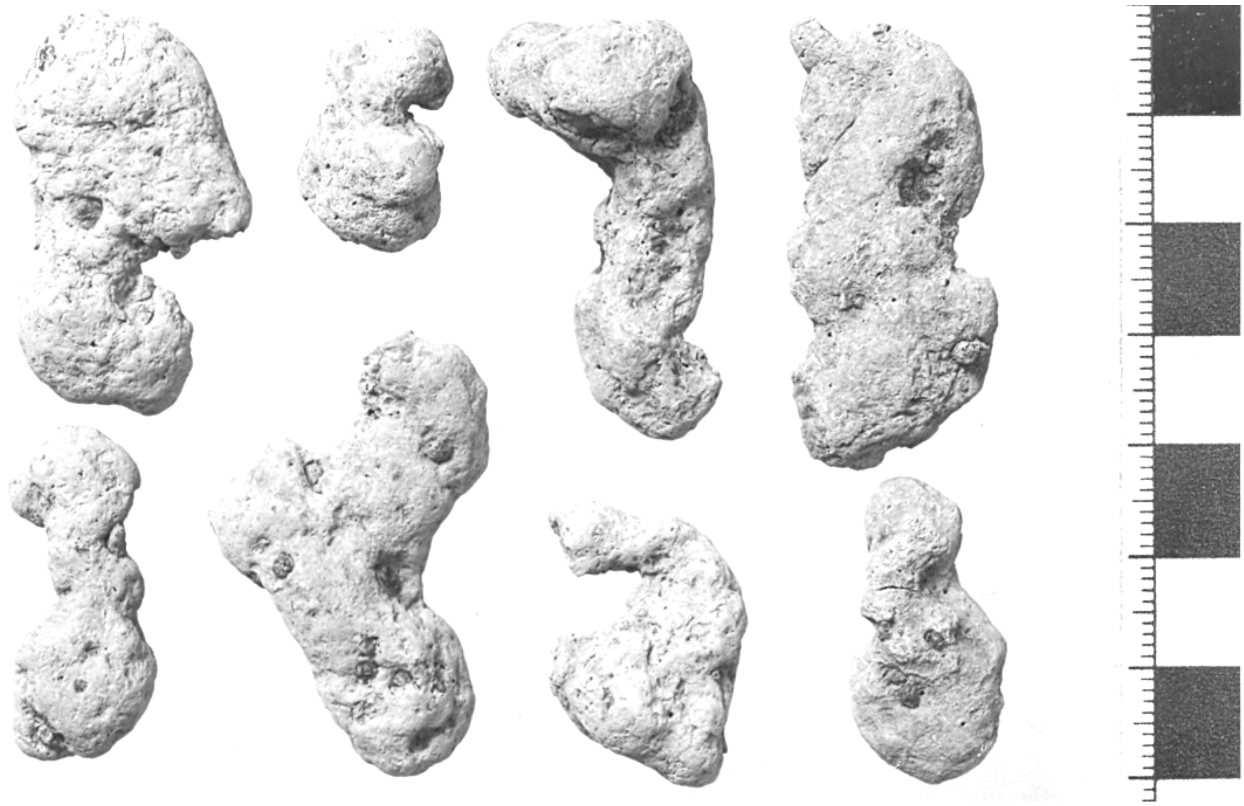

Figure 6. Cake Pill. Selected concretions, with scale marked in centimetres.

categories. The concretions take a number of forms, including root tubules. Microconcretions of diagenetic mixed iron sulphides, but without siderite, are commonly seen in anoxic intertidal and shallow-marine sediments, as reported by Bertolin *et al* (1995) from the modern sediments of the shallow, tide-swept Lagoon of Venice.

MID HOLOCENE (Awre)

In the Severn Estuary Levels, interbedded estuarine silts (mudflats/salt marshes) and peats (organic marshes) are normally restricted to the mid Holocene portion of the Wentlooge Formation. In many places one or more of these interbedded silt units shows tidal laminations and seasonal banding (Allen 2004, Allen and Haslett 2006), on scales suggesting that deposition occurred at rates measuring centimetres annually. Each tidal lamina, taking a sub-millimetre to millimetre scale, is a couplet formed of a sharp-based lower part of clean, well-sorted silt to very fine-grained sand that grades up into an overlying, clay-rich layer.

Evidence for the local calcification of the mid Holocene laminated and banded silts is common along the shores of the Levels. Typical are exposures around the tip of the Awre peninsula (Figure 1) in the inner estuary (SO 7107, 7208), where the local bedrock is formed by the early Jurassic Lower Lias. Here calcification takes the form of substantial, fully-cemented concretions of fantastic, flattened, often branching, smoothly rounded form which grew parallel with the bedding (Figure 5A-C), like similar forms recorded by Knight (1998) from an Irish glaciofluvial sand. Typically, each concretion from Awre embraces several to many tidal laminae, the calcite cement, in the form of micrite grading to microspar, firmly binding the silt and clay portions equally. Piercing the concretions are scattered, occasionally branching, cylindrical voids up to a few millimetres across lying at steep angles to the bedding. These are now largely empty, but many contain an organic lining or loosely arranged fibres, suggesting occupation initially by plant roots.

The presence of these concretionary forms points to the local mobilisation of calcite, probably by the action of acidified waters acting on the mainly bioclastic debris which forms a significant proportion of the sediment as deposited. That mobilisation occurred entirely within the sequence is suggested by the local decalcification of laminated and banded mid Holocene silts many decimetres thick (eg Allen and Haslett 2006). When mobilisation took place is uncertain, but the process could have been penecontemporaneous, given the evidence for its operation today at sites of active, albeit very slow, tidal sedimentation on some marshes (see below) and the presence of what appear to be root channels. As the silty-sandy parts of the laminae are much more permeable than the clayey portions, it is not surprising to find that the concretions grew most rapidly parallel with the bedding.

LATEST HOLOCENE (Cake Pill)

The estuarine wetlands underlain by the Wentlooge Formation became embanked from the Roman period onward, but such active marshes as remained continued to evolve as the coast experienced change. At least three, and possibly four, substantial post-embanking silt units can be identified in the Severn Estuary Levels, termed the Rumney (?bipartite), Awre and Northwick Formations (Allen and Rae 1987), each following an erosional episode on the margins of the estuary, representing marsh initiation during the seventeenth-eighteenth century, and then again in the late nineteenth century, and the early-mid twentieth century.

The Rumney Formation, of commonly laminated pale brown silts, underlies the highest marshes in the area, at a level only a few decimetres below that of the highest astronomical tide. Consequently, these marshes are inundated by relatively very few tides, and at certain stages in the tidal cycle can remain dry for many weeks. There are almost no natural exposures of the higher parts of the Rumney Formation but the construction in 1991-2 of a new seabank, sluice and set of drains at Cake Pill (*c*. SO 563881), south of the First Severn Road Bridge, provided an excellent set measuring up to 2 m or more in depth. Carbonate concretions appear at two, closely-spaced horizons throughout these sections.

A typical profile of concretion abundance appears in Figure 5D, based on dried bulk samples of sediment that were the disaggregated and wet-sieved. The representative concretions shown in Figure 6 are irregular and seldom more than a few centimetres long. Most lie parallel with the lamination but a few, associated with rootlets, are elongated vertically. A representative number were digested in dilute hydrochloric acid, revealing an average content of insoluble matter of about 30 wt. %. Thin-sections of representative concretions show quartz silt and other detrital minerals thinly dispersed in a predominant matrix of micritic calcite with occasional irregular patches and veins of microspar, and small root channels lined by plant tissue. A few roughly concentric and occasionally radial, open fractures are also seen. X-ray diffraction analysis of five representative concretions gave the following compositional ranges: quartz (16.1-25.7%); clay minerals (illite, chlorite, kaolinite, occ. mixed layer)(6.3-11.0%); feldspars (1.5-5.2%); calcite (56.5-69.1%); dolomite ($CaMg(CO_3)_2$, 1.0-2.1%); siderite (0.9-1.5%); and pyrite (one sample: 2.6%).

The low proportion of detrital material in the concretions, the high content of carbonate minerals, and the presence of roughly concentric fractures all point to the displacive introduction of the micrite seen. Macroscopically and microscopically, the concretionary deposits have some similarity with the early stages in the development of pedogenic calcretes (Wright 1986), formed in areas of warm climate and seasonal rainfall where downward leaching under oxic conditions followed by precipitation can occur. In the case of the Rumney Formation, the carbonate concretions are likely to record the mobilization of mainly detrital bioclastic calcium carbonate within the deposits of this high marsh. Typically, Severn Estuary silt has a carbonate content of about 10%, mostly shell fragments but with some calcite-dolomite derived from the Trias, whereas Crooks (1999) found that the uppermost sediments of the Rumney Formation are either deficient in or lacking calcite because of decalcification. The appearance of the concretions at two main levels suggests that there were abrupt changes in the porewater regime during the growth of the high marsh at Cake Pill.

REFLECTIONS

Much more work is needed before firm

conclusions can be drawn about the origins of the various forms of carbonate diagenesis described above and about their stratigraphical and geographical distributions within the later Quaternary sediments of the Severn Estuary Levels. What does seem clear, however, is that carbonate diagenesis has occurred under anoxic as well as oxic freshwater conditions. Although no examples are included above, there is every reason to suspect that early sulphide diagenesis, as in the Lagoon of Venice, is also occurring in the saline intertidal mudflat and sandflat deposits of the Severn Estuary and in many of the most recent saltmarsh sediments. The muds in particular have on deposition a total organic content of a few percent and typically are blackened (ie reduced) below a depth of a centimetre or so from the sedimentary surface. The various diagenetic processes that operate or operated in the Severn Estuary Levels involve the mobilisation of elements such as Ca, Mg, Fe, Mn and P, and some are likely to be bacterially mediated. Depending on their character and context of operation, they have the potential to preserve, modify or destroy materials of environmental and archaeological significance. As such, it would seem desirable to secure a better understanding of their character and role in the archaeologically-rich Severn Estuary Levels.

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