The occurrence of calcium phosphate in the Mesozoic and Tertiary of Eastern England

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Abstract: Phosphate is a minor component of Mesozoic and Tertiary formations. It occurs widely scattered as nodules in argillaceous sediments, but is commonly concentrated in pebble beds and may be found replacing fossils. Phosphatic animal remains are rare and commonly occur immediately above major discontinuities, and fossilised animal faeces (coprolites) are extremely rare. Phosphatic pisoliths occur at only one horizon.

In Eastern England calcium phosphate occurs as coprolites, bones, fossil replacements, ill-defined impregnations, nodules, pebbles, pisoliths and hardgrounds in Mesozoic and Tertiary strata. Many geologists (*eg*. Horton *et al*., 1974, p.35) have been guilty of imprecise use of these terms. Using local examples it is possible to obtain a clear understanding of the diverse origins of these deposits.

Phosphorus occurs as a minor element in igneous rocks. Weathering and erosion result in transfer of the element within detrital grains and in solution. In marine environments, the phosphorus may be concentrated by physical, chemical and biological processes, 'precipitated' as calcium phosphate nodules, bones and coprolites and subsequently reworked as pebbles.

Coprolites

Coprolites are trace fossils made up of faecal material. Duffin (2009) records how in the 18th century a group of ornamented stones from the Chalk were thought to be cones and fruits of trees. It was Buckland (1822, 1823) who, on the basis of his work on Kirkdale Cave, recognised fossil hyaena faeces. With others, he found faeces in the basal beds of the Lias, the basal Rhaetic Bone Bed and the basal conglomerate of the Carboniferous Limestone. He concluded that the Cretaceous fossils were also of faecal origin and should be referred to as *Copros iuloides*. Buckland's final proposal was to "include them under the generic name of Coprolite", from the Greek, cous = dung, lithos = stone (Duffin, 2009).

The early 19th-century fossil collectors of Lyme Regis found unusual ornamented " Bezoar stones" from the Lower Lias (Buckland, 1829). These were recognised as faeces by Buckland (1836) who described them as occurring at some levels as 'being so abundant that they lie like … potatoes scattered on the ground'. This contrasts with the experience of the author and colleagues who have spent careers studying Mesozoic clay formations in exposures and borehole sequences without finding a coprolite. The author's only possible candidate is a faecal pellet from the Lower Lias. Such pellets are small, fawn-coloured cylinders, 1-2 mm in diameter and 4-5 mm long. Although fragile, they have linear ridges that are suggestive of extrusion, and they occur in association with scattered simple ornamented plates, possibly of crustacean origin.

Figure 1. *Coprolites from the basal Scunthorpe Mudstone Formation, Lias Group at Lyme Regis, Dorset (all photo courtesy of British Geological Survey).*

The success of the early coprolite collectors may reflect the coprolites' original large numbers and their subsequent concentration by selective marine erosion with wave sorting of the dense material (Figs. 1 and 2). In ancient brick pits, clay was removed in layers, thereby exposing bedding planes and their contents much more accessibly than in the few pits working today with mechanical excavation and vertical sections. Ford and O'Connor (2009) conclude that 'most coprolites come from the larger marine reptiles or fish which fed on their smaller brethren and concentrated phosphate in their faeces'.

In the mid-19th century, phosphate was worked commercially from several horizons. These were

Figure 2. *Small (fish) coprolites from Lyme Regis.*

described informally as 'coprolite beds' and 'coprolite workings', which are misnomers since the beds contain few, if any, coprolites. The error started with Henslow (1846) who, although writing on concretions in the Red Crag at Felixstowe, was inclined to describe them as 'water-worn pebbles' but wrongly concluded that they were coprolites. The error was recognised by Charlesworth (1868, p.577): ' a mistake, but one, perhaps, of the happiest mistakes ever made by a man of science; for had not Professor Henslow believed these stones to be coprolites (fossil dung) he would never have had them analysed, and the phosphatic nature and consequent agricultural value of these stones might possibly for centuries to come remain unknown'.

Bones

Phosphatic animal remains, including those of dinosaurs, mammals and fish (bones and teeth), are found in the lag gravels associated with major disconformities. Most were derived from the erosion of older sediments, but in the case of the youngest strata some may have been penecontemporaneous

Nodules

Nodules may be irregular, spheroidal, or ellipsoidal and are commonly composed of calcite, siderite, silica, gypsum or phosphate. Concretions have a similar origin, but are larger and most commonly calcareous. Nodules are autocthonous, in that they are enclosed in the sediment within which they formed.

Unconsolidated clay-rich sediment may be described as a chemical soup. Phosphorus may occur within decaying marine organisms, within mineral grains, loosely bound within the structure of clay minerals or as phosphate ions in solution. During diagenesis, compaction of the mud mobilizes the pore-water which becomes increasingly enriched with minerals. These react and attempt to reach equilibrium in the evolving chemical environment. Variation in chemical composition, perhaps enhanced by the presence of decaying organic matter, creates chemical gradients with migration of phosphate-rich solutions and the precipitation of calcium phosphate at nodal points, commonly organic detritus and shells.

Phosphatic nodules are most common in marine Mesozoic and Tertiary mudstones. They may be isolated and scattered throughout the sediment, but are commonly located on specific bedding planes. The latter may be sufficiently abundant to constitute 'a bed'. The paramount factor is that the nodules remain *in situ*, in their position of growth. Many nodules are structureless, showing no evidence of their initial trigger to growth, whereas others may partially enclose or totally replace organisms.
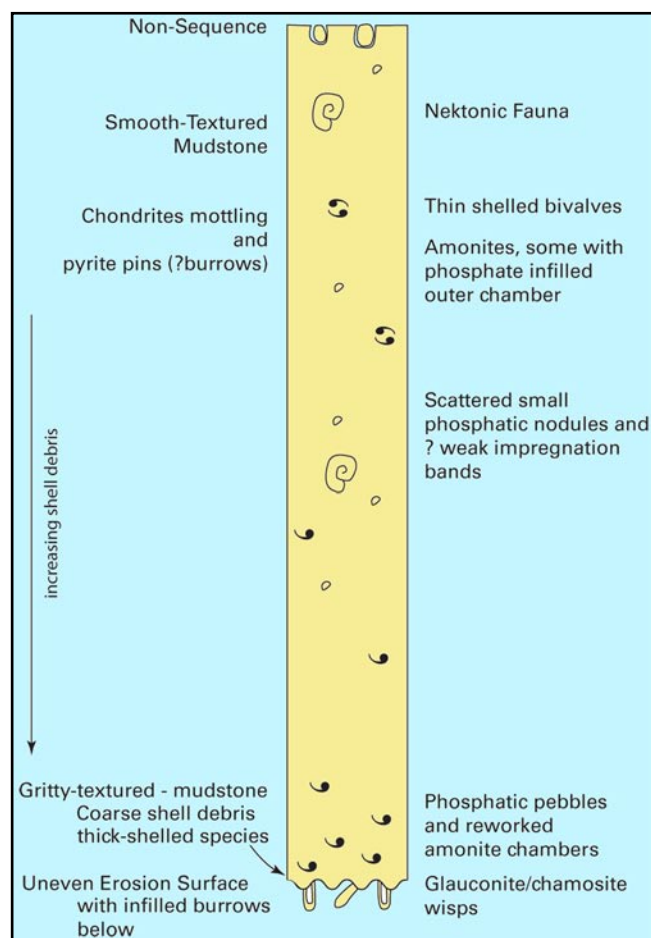
Pebbles

These are fragments, 2-64 mm in diameter, which have been separated from their source rock, abraded and rounded during transport to a new location.

Pebbles are allocthonous, i.e. separated in time and space from their source rock. Generally the term is applied to hard rock fragments derived from strongly indurated strata. It can also be applied to debris of weakly consolidated sediments in which diagenesis is well advanced and nodules have already formed. Thus eroded nodules become pebbles with minimal abrasion and transportation.

Breaks in sedimentation within the Mesozoic range from geologically short-lived hiati, between beds within formations, to increasingly longer gaps between formations, groups and systems. The breaks may be marked by a burrowed surface, a lag deposit (gravel), an inter-formational conglomerate, or a major erosion surface overlain by far-travelled exotic pebbles. All types occur within England, and phosphatic pebbles may be a significant component in them. Phosphatic pebbles have been described from a number of horizons.

Rhythmic sedimentation is common in Mesozoic mudstones, and is particularly well developed in the Gault (Gallois and Morter, 1992). An idealized Gault rhythm starts with a period of increased current activity causing erosion of the underlying bed, and then the development of an inter-burrowed basal surface (Fig. 3). This may be glauconitised or phosphatised, and is overlain by a silty, shelly, pebbly mudstone containing

Figure 3. A typical sedimentary rhythm that is present in many Mesozoic marine mudstone sequences (after Gallois and Morter, 1982).

waterworn phosphatic pebbles, some with encrusting organisms, and others with superficial micro-borings, exhumed burrow-fills, derived belemnites, oysters, etc.. In time, current activity declined, the silt content decreased upward, fossils were preserved and phosphate nodules were precipitated within the clay sediment. These rhythms are only 1-2 m thick. Each started when the mudstone was partly consolidated, and any increase in current activity caused erosion, downcutting and winnowing of the newly formed nodules and thicker shells. The phosphatic nodules were eroded with minimal abrasion, and further reworking may have enhanced the phosphatisation. The presence of encrusting organisms and microborings confirm the conversion of nodules to pebbles.

Hardgrounds

These are indurated surfaces developed within recently lithified sediments, commonly limestones, during subsequent periods of very limited sedimentation and reworking. These phosphatic impregnations have irregular forms and some have a complex history of formation. They occur in the Chalk Rock. Three 'indurated phosphatic mudstone' horizons have been recognised within bed 15 of the standard Upper Gault sequence in the Arlesey borehole, Bedfordshire (Woods *et al*., 1995). Further details are not available and specimens were not retained.

Pisoliths

Calcareous ooliths and pisoliths are generally deposited as calcite in a high energy marine environment. These sediments are commonly converted to limestones which may, very rarely, be subsequently altered to phosphatic material. An extremely unusual example of 'free' phosphatic pisoliths occurs in the local Whitby Mudstone Formation (Upper Lias).
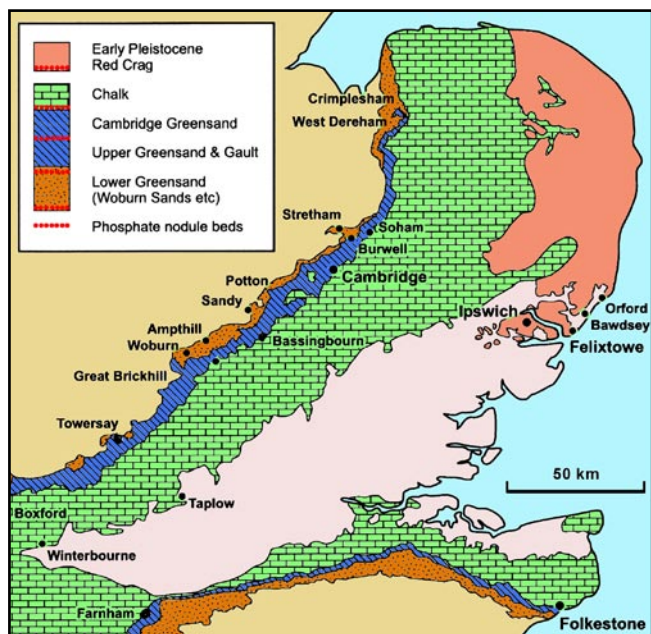

Figure 4. *Some of the main sites of the former extraction of 'coprolites' (after Ford and O'Connor, 2009).*

Age	Formation	
Neogene	Red Crag	E*
	Coralline Crag	E
Upper Cretaceous	Cambridge Greensand	E*
Lower Cretaceous	Upper Gault	E
	Lower Gault	E
	Woburn Sands	E
Upper Jurassic	Portland	E
	Kimmeridge Clay	
	Ampthill Clay	
	Corallian (Beckley Sand)	
Middle Jurassic	Northampton Sand	
Lower Jurassic	Whitby Mudstone	
	Marlstone Rock	
	Charmouth Mudstone	
	Scunthorpe Mudstone	

Figure 5. *Formations that contain significant amounts of phosphate. E = formation from which phosphate has been extracted; E* = major source of phosphate.*

Stratigraphic distribution

The various occurrences (Fig. 4) can be related to their depositional environments and then reviewed in stratigraphical order (Fig. 5).

Triassic
Penarth Group, Westbury Formation

The presence of coprolites in the 'Rhaetic Bone Bed' which occurs at or near the base of the Westbury Beds, has been known since the early 19th century (Buckland, 1829). Duffin (1979) has recognised five morphological types from the British exposures. Types with distinct geometric form, spiral patterns, or protruding bones are clearly identifiable. Others may vary in form and could be mistaken for spheroidal or mis-shapen nodules, phosphatic pebbles or phosphatised fossils.

Fish teeth have been described from the Westbury Formation at Barnstone (Sykes, 1979) and fossil vertebrates from the Newark area (Martill and Dawn, 1979). Resurvey of the Nottingham district proved several phosphate bearing horizons ('bone beds') in the Westbury Formation (Howard *et al*, 2008). A siliceous sandstone near the base contains coprolites and vertebrate remains. A bed at a higher level contains abundant fish and reptile remains, rolled phosphatised coprolites and quartz granules. Phosphatic pebbles and nodules occur in all beds.

Jurassic
Scunthorpe Mudstone Formation

This formation was formerly known as the lower part of the Lower Lias. The two youngest units, the Beckingham and Foston Members contain separate beds of 'calcareous nodules' and 'phosphatic nodules', with the phosphatic nodule beds occurring beneath

locally persistent limestones (Brandon *et al*, 1990). The oldest underlies the Stubton Limestone, a ferruginous bioclastic limestone with limonitic ooliths and abraded and bored *Gryphaea*, and here contains minutely bored small phosphatic pebbles. Bored phosphatic 'nodules' also occur below the Fenton Limestone, while those below the Highfield Limestone are associated with bored and reworked ammonites. The Highfield Limestone contains *Gryphaea*, some abraded and bored, and also reworked phosphatic pebbles. Although the phosphate is described as nodules, the evidence of boring and transportation suggests that some may be pebbles.

Charmouth Mudstone Formation

In the Melton Mowbray district, the basal Glebe Farm Bed is a thin ironstone with reworked phosphate and calcite mudstone nodules that rests on an erosional surface (Carney *et al.*, 2002).

A borehole investigation for an underground gas storage scheme at Chipping Norton proved both the Scunthorpe and Charmouth Mudstone Formations of the Lower Lias (Horton and Poole, 1971). Most of the mudstones were not cored, but geophysical logs revealed three marker horizons within the Charmouth Mudstone. These were arbitrarily named, in increasing age, as the 100, 85 and 70 markers. Cores taken at these horizons revealed that the 70 marker lies within the *Uptonia jamesoni* zone, the 85 within the *Tragophylloceras ibex* zone, and the 100 at the boundary of that zone with the *Prodactylioceras davoei* zone. The geophysical signatures resulted from limestones and marls within the predominantly clay sequence. The argillaceous strata showed evidence of rhythmic sedimentation, but this was less clear in the calcareous beds. The base of an ideal rhythm is defined by a pause in the sedimentation, sometime with erosion and U-shaped burrows (Fig. 3). This is overlain by coarse, shell-debris-rich mudstones and limestones with thick-shelled bivalves typical of deposition in a high-energy environment. Ferruginous and phosphatic nodules and pebbles were recorded, but none was analysed. The amount and grain-size of
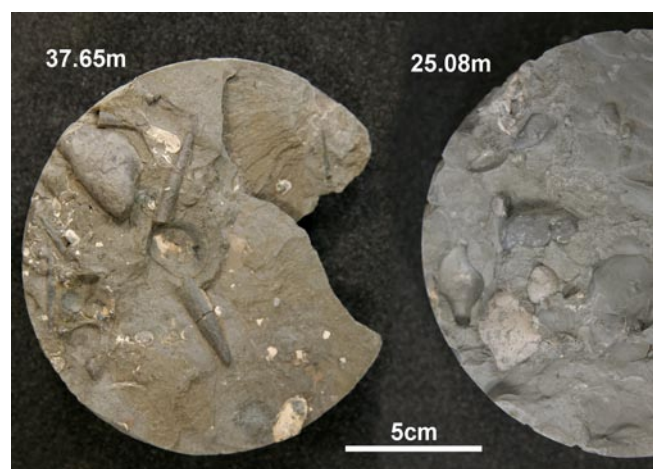
Figure 6. Phosphatic pebbles with belemnites, bivalves, shell debris and chamosite silt, marking the base of two sedimentary rhythms within the Charmouth Formation at indicated depths in the Thorpe-by-Water Borehole, Rutland.

the shell debris decreases upward as the mudstones pass into smooth-textured mudstone with *Chondrites* mottling and immature bivalves.

The Charmouth Mudstone was proved in a series of cored boreholes, drilled on behalf of the British Geological Survey in the Buckingham-Huntingdonshire area. The youngest beds of the Charmouth Mudstone (*Prodactylioceras davoei* zone) consist of grey mudstone with a rhythmic pattern of sedimentation. The base of each rhythm is marked by a burrowed surface overlain by thin chamositic silt with black phosphatic pebbles, some of which were chambers of the zonal ammonite *P. davoei* (Fig. 6). This is overlain by smooth mudstone with scattered shells including ammonites. The calcitic shells of the latter were crushed during compaction except for the last body chamber which was sometimes infilled with phosphate. Sedimentation continued until a change in bottom conditions when a period of increased current activity resulted in erosion of the recently deposited clay, thereby revealing the nodular ammonite fragments. These suffered minimal abrasion during their transformation into pebbles and deposition at the base of the next rhythm. The Charmouth Mudstone passes up into the overlying Dyrham Silt Formation, and the base of the latter was drawn at the top of the last rhythm with a phosphatic *P.davoei* pebble.

Marlstone Rock Formation

Along its outcrop from Banbury to Lincolnshire, the base of the Marlstone Rock is locally marked by a conglomerate with discoidal pebbles, up to 80 mm diameter, of pale brown, phosphatic siltstone-mudstone (Fig. 7). These were derived from the underlying Dyrham Silt Formation, which is relatively soft, and may have been locally strengthened by phosphatisation during erosion. High density black phosphate pebbles have not been found.

Whitby Mudstone Formation

This formation (previously the Upper Lias) was well exposed during the construction of the Empingham Dam to impound Rutland Water, where it illustrates the diversity of phosphate deposition (Horton and
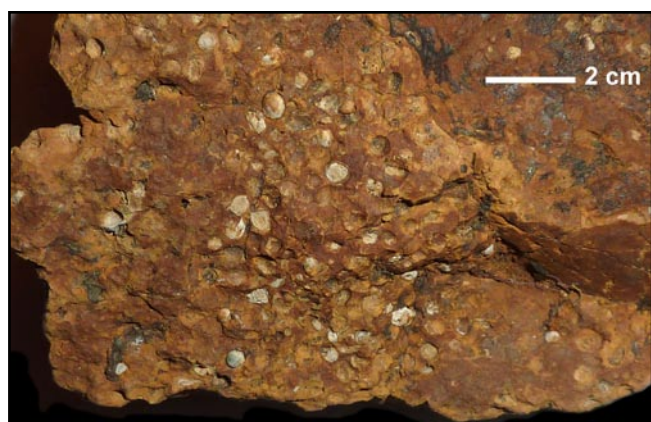

Figure 7. Basal conglomerate of the Marlstone Formation at depth 5.4 m in the BGS Thorpe-by-Water Borehole, Rutland; sawn vertical surface with dark belemnite platy phosphatised siltstone pebbles from the underlying Dyrham Formation.

Coleman, 1977). The basal Fish Beds Member is a very thinly laminated mudstone, with bedding planes rich in immature *Posidonia* spat with phosphatic chitinous insect and fish remains. The top bed of the succeeding Cephalopod Limestone Member is the Pisolite Bed, a micritic limestone and marl. Within it, scattered large pisoliths were originally deposited as calcite and formed in a high energy environment (Fig. 8). They were replaced by phosphate, presumably in a quiet-water situation, and then transported and deposited with the calcareous micrite in which they now float. The micritic matrix is structureless with no evidence of bioturbation. The presence of an extremely small eroded fragment comprising phosphatic ooliths and phosphatic matrix indicates that in at least one (so far unique) area a second stage of phosphatisation preceeded final deposition (Fig. 9).

Phosphatic nodules are scattered in the overlying mudstone which also contains weakly impregnated phosphate beds, scattered nodules and a bed with many nodules, the 'Smartie' Nodule-Bed. Higher in the sequence the Ammonite Nodule Bed is a hard calcareous mudstone containing wisps of fine shell debris, calcareous nodules (up to 70 mm across) and ammonites, bivalves and belemnites, some of which are phosphatised. A hiatus at the base is marked by a bed of coarse shell-debris, which extends down in burrows into the underlying smooth-textured mudstone

The mudstones at the top of the Whitby Mudstone are slightly silty with scattered small phosphatic nodules. They contain evidence of a second hiatus with a major burrowed surface overlain by a thin lenticular conglomerate that passes laterally into silty shell-debris partings. Pebbles vary in size and shape, the more rounded are more highly phosphatic, and are probably reworked nodules (Fig. 10). Large irregular pebbles are phosphatised limestone concretions. The associated fossils include thick-shelled oysters, belemnites and rare rhynchonellids, set in a glauconitic pyritic sandy matrix. Some of the pebbles are bored, and parts of the
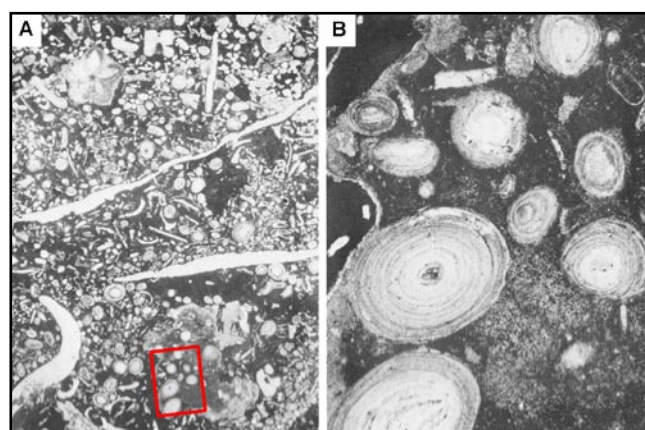
Figure 9. Photomicrographs of thin sections of ooids from the Cephalopod Limestones Member of the Whitby Mudstone, in the BGS Apley Barn Borehole, Witney, at a depth of 51.5m. A = shell-debris oolitic sideritic micritic limestone, with a pentacrinoid ossicle top left. B = 10x enlargement of the red box in A within a derived fragment of finely crystalline cellophane (phosphate) with unsorted phosphatic ooliths having concentric layers a few microns thick.

top of the bed are encrusted with calcareous algae. This non-sequence and associated lag gravel has not been described for any other Upper Lias site. Despite daily examination and mapping of the ground beneath the proposed dam during its construction, not one coprolite was discovered (Horswill and Horton, 1976).

Northampton Sands and Scissum Beds

The Northampton Sand Formation and its lateral equivalent in the Cotswolds rest disconformably upon the Whitby Mudstone Formation (formerly Upper Lias). The basal pebble bed contains phosphatised pebbles, some of which show shallow borings, and black phosphate pebbles. Because of its high phosphorus content, it was left as the floor beneath the ore-grade material of the Northampton Sand ironstone quarries. Although commonly much less than 30 cm thick, it provided a base for the rail track used by the wagons to transport the iron ore. The Whitby Formation was commonly exposed in shallow drainage ditches.

Oxford Clay Formation

Alan Dawn reported that he had collected coprolites from the Stewartby Member (formerly the Lower Oxford Clay) in brick pits near Peterborough. In his search for reptile skeletons he examined the abandoned steep quarry faces for protruding bones. A major mechanical excavation down from the ground surface to one such prospect was successful (Martill *et al*., 1979), wherein a final excavation by hand revealed a bedding plane with skeletons of reptiles and fishes and small coprolites up to 20 mm in diameter. These were associated with small rods, 1-2 mm in diameter and up to 5 mm long, that were similar to the probable faecal remains described herein from the Charmouth Mudstone Formation. Alan Dawn collected one large coprolite and many small specimens from the rain-washed weathered spoil heaps on the quarry floor.

Figure 8. Pisolite Bed in the Cephalopod Limestones of the Whitby Mudstone at Holwell North Quarry, Melton Mowbray. Phosphatic pisoliths 'float' in weathered micritic matrix of the limestone.

Corallian Formation, Beckley Sand Member

Small rounded phosphate pebbles in association with chert and quartz have been recorded in thin, localised lag gravels near Oxford (Horton *et al*., 1995).

Ampthill Clay Formation

At least five phosphatic 'nodule' beds occur in the Ampthill Clay in the Wash area (Gallois and Cox, 1977). Each bed forms the base of a rhythm is defined by a basal, burrowed erosion surface. This is overlain by a gritty, shell-rich clay with thick-shelled oysters, commonly encrusted with serpulids, and rolled fossil fragments. The sequence continues progressively upward into smooth-textured mudstone. Each rhythm is thought to represent an increasing depth of water and progressively quieter bottom conditions.

The phosphatic nodule beds are said to contain 'phosphatic chips' and one contains 'phosphatised ammonite and bivalve debris', another 'rolled belemnites and oysters, the beds are shown to rest on intra-formational unconformities (Gallois and Cox, 1977). Given this evidence of erosion, it may be more appropriate to refer to the nodules as 'pebbles'. In the Thame district, the equivalent beds contain small rounded to angular phosphatic clasts, some of which are internal moulds of bivalves or ammonite body chambers (Horton *et al*., 1995).

Kimmeridge Clay Formation

In the Thame district, a phosphate pebble bed at the base of the Kimmeridge Clay cuts down to various levels in the topmost beds of the Ampthill Clay (Cox and Sumbler, 1991). The Lower Lydite Bed marks a second erosional event. This thin bed again contains phosphatised casts of bivalves and ammonite whorl chambers with sporadic small pebbles of lydite (black chert) and quartz. There is some evidence that the

Figure 10. Impersistant conglomerate in the upper part of the Whitby Mudstone Formation, at Empingham Dam site, Rutland Water. The upper surface (right) consists of shells, including belemnites and small pebbles, whereas the lower surface (left) includes large pebbles with borings and belemnites. The smaller fragment contains shell debris and phosphatised pebbles that have darker rims and enhanced radioactivity.

phosphatic clasts were phosphatised before erosion from *Pectinatus* zone sediments (Cox *et al*., 1990).

Portland Formation

In the Thame district, the base of the Portland Formation is marked by an erosion surface (Horton *et al*., 1995), Commonly this is overlain by the Upper Lydite Beds, which are limestones characterised by small lydite pebbles associated with quartz and quartzite, and also rare black phosphate pebbles that include casts of ammonite whorl fragments.

Cretaceous

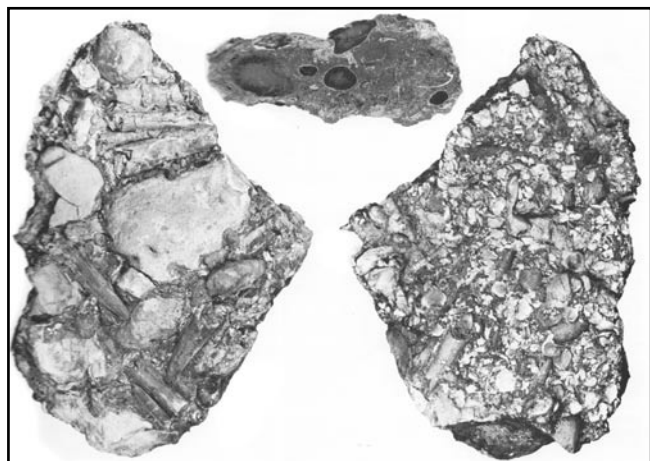## Lower Greensand, including Woburn Sands

In the Leighton Buzzard District the Lower Greensand comprises the thick Woburn Sands division and the thin, overlying Junction Beds. It rests unconformably on undivided West Walton and Ampthill Clay formations of Upper Jurassic age.

Phosphatic pebbles have been recorded in at least two levels within the Woburn Sands (Sheppard-Thorn *et al*.,1994). They were formerly extracted for fertilizer at localities between Little and Great Brickhill, Bedfordshire. Hereabouts a basal sandstone contained well-preserved, reworked phosphatic bivalves and brachiopods with whorl fragments (chambers) of pavlovid ammonites derived from the Jurassic Kimmeridge Clay. Higher in the Woburn Sands, an erosion surface locally cuts out 3 m of strata that overlie a major seam of Fuller's Earth. Above it a basal pebble and grit lag deposit includes dark lydite and quartz pebbles and also phosphatic ammonite fragments of Upper Jurassic provenance.

There was a break in sedimentation after the deposition of the Woburn Sands. Subsequently the sea transgressed a gently uneven surface of the Woburn Sands and deposited the Junction Beds, an extremely variable and laterally impersistent sequence of lithologies. They include the marine Shenley Limestone, which contains pockets of ironstone and passes laterally into glauconitic sandy marls with phosphatic nodules and ironstone fragments. These beds have not been exploited for phosphate; they are overlain by the Lower Gault.

In the Cambridge District the Woburn Sand facies is replaced by typical, marine, glaucontic Lower Greensand that overlies the Kimmeridge Clay non-sequentially. Between Westwick and Cottenham, northwest of Cambridge, 'the basal 1.2-1.5 m of the Lower Greensand comprises brown sand and clayey sand with phosphatic nodules, derived Jurassic ammonites, indigenous fossils, ironstone nodules and clay lumps with secondary calcite nodules' (Worssam and Taylor, 1969). This bed was worked for phosphate.

To the northeast, near Upware, Keeping (1868) described an unlocated excavation that showed 2.56 m of Gault Clay with 0.13 m of phosphate nodule bed above the base. Keeping's diagram lacks a scale but shows the Gault overlying Lower Greensand that rests

on Kimmeridge Clay. Worssam and Taylor (1969, p.31) reinterpreted the sequence to show about 0.45 m of red and yellow sand, overlying an Upper Nodule Bed about 0.3 m thick, a pebbly sand with pale phosphate of lime, pebbles of chert etc., and many well preserved brachiopods. This rests on 0.45 m of red and yellow loose sand, which in turn overlies the Lower Nodule Bed, also about 0.3 m thick, which is a pebbly sand and conglomerate with nodules of phosphate of lime, pebbles of chert, etc, with many well preserved molluscs, overlying Kimmeridge Clay. It is probable that all three 'phosphatic nodule' beds were exploited. Keeping (1883) noted that the fauna of the Lower Bed included bones and teeth of reptiles and fishes, brachiopods, sponges, bryozoa, a few echinoids, annelids and a rich assemblage of molluscs. Worssam and Taylor (1969) described the bed as a condensed deposit, representing several Aptian ammonite zones, with fossils derived from Oxford Clay, Ampthill Clay, Kimmeridge Clay, Portland Formation and Sandringham Sands (uppermost Jurassic). There is no mention of coprolites.

Gault and Upper Greensand Formation

The Gault Formation crops out below the Chalk escarpment from Wiltshire to Norfolk. It rests non-sequentially on the Lower Greensand and overlaps it to rest unconformably on Jurassic strata and the Palaeozoic rocks of the buried London Platform. It consists almost entirely of richly fossiliferous marine mudstones. The Lower Gault mudstones are dark grey, whereas those of the Upper Gault are paler grey, more calcareous and silty. Gallois and Morter (1982) divided the formation in East Anglia into nineteen beds on the basis of lithological and faunal characteristics. Thirteen of these have clearly defined erosional bases, and the sequence could be described in terms of a repeated ideal rhythm. The base of each unit was defined by a non-sequence: an extensively burrowed, phosphatised and possibly glauconitised erosion surface (Fig. 3). This is immediately overlain by siltstone or silty mudstone with abundant shell debris, fragmentary shells, abraded belemnites and black phosphatic pebbles including reworked phosphatised ammonites. The overlying mudstone becomes slightly paler and less silty upward. Shells are commonly crushed and preserved as aragonite. There is no mention of nodules in the upper part of the rhythms.

At many levels in the Thame District, phosphatic nodules grew *in situ*, commonly around fossils or burrows (Horton *et al*., 1995). Additionally, erosive non-sequences are generally marked by bands of bluish-black phosphatic pebbles. Most of these are nodules eroded from underlying beds, which have undergone further phosphatisation during reworking. These beds were worked at three localities between Thame and Aylesbury, probably from near the base of the Upper Gault. At Ford (SU790694) there were two seams, possibly within 1 metre, the main seam being 10 cm thick (Jukes-Browne and Hill, 1900). Pebbles

collected from the restored soil surface during the resurvey were irregularly shaped; many are internal moulds of ammonite segments or bivalves, most show evidence of abrasion, and many are bored or show signs of encrusting epifauna (Horton *et al*., 1995).

In the Leighton Buzzard district phosphate was dug from high levels in the Upper Gault and Upper Greensand (Shephard-Thorn *et al*., 1994; Jukes-Browne and Hill, 1900). In the Sundon borehole, phosphate nodules occur in both the Upper Gault and the overlying Upper Greensand. In the former, some of the more phosphate-rich beds rest on an erosion surface and at one level contain oyster-encrusted nodules. At Buckland and Chaddington, near Tring, Jukes-Browne (1875) described excavations that yielded beds with numerous black phosphate nodules. The phosphatic material at both these sites may actually be pebbles.

Despite the large number of cored boreholes drilled through the Gault and examined by the British Geological Survey, not one coprolite has been recorded. Curated specimens from the boreholes of Arlesey (TL189346) and the Ely-Ouse No.14(TL696812) have phosphatic trace fossils within bed 16 of the standard Upper Gault sequence. These are crushed trace fossils that were originally cylindrical burrows 15 mm in diameter and lined with undigested organic remains (Fig. 11). These have a clear amber-like preservation and include fish spines and scales with growth rings. A similar fossil was found in a borehole at Duxford (TL481454) near Cambridge. Phosphatic nodules and pebbles occur throughout the formation.

Cambridge Greensand Formation

This formation was the major source of commercial phosphate. In the Chilterns a thin bed, the Glauconitic Marl, occurs at the base of the Chalk and locally contains small brown phosphatic pebbles (Horton *et al*., 1995). Traced northeastward in the Leighton

Figure 11. Trace of a burrow lined with fish and crustacean debris, in the Upper Gault at a depth of 132 m in the Duxford Borehole, in core that is 76 mm in diameter.

Buzzard district it proved difficult to map the boundary where silty textured Glauconitic Marl overlies silty glauconitic mudstones of the Upper Greensand. The lateral transition from Glauconitic Marl to Cambridge Greensand is near Shillington, Bedfordshire, where pale phosphate pebbles characteristic of the Glauconitic Marl are replaced by dark phosphate pebbles.

For many years, the age of the Cambridge Greensand was controversial. The published evidence shows that the Cambridge Greensand is a basal conglomerate of the Chalk Group. It is a condensed deposit and the basal bed contains moulds and casts of fossils including ammonites (Fig. 12). Casey (in Edmonds and Dinham, 1965) concluded 'it is clear that the phosphatised faunas for which the Cambridge Greensand is famed contain no closely datable elements that are not Upper Albian. Though it may well be true that the deposit was finally laid down in Cenomanian times'. Hart (1973) concluded on the basis of foraminiferal assemblage zones, that some parts of the Cenomanian stages were absent. Cambridge Greensand contains a remanent fauna of phosphatized fossils characteristic of the higher Gault and Upper Greensand and an indigenous Cenomanian calcareous fauna (Hopson *et al*., 1996).

The importance of this non-sequence was noted by Seeley (1866) who described the overlying lithology as dark nodules in a soft matrix of marl and glauconite 15-30 cm thick resting on an irregular surface. It contains a few large stones up to 30 cm in size, including granite, hornstones, quartzites and sheared rocks, some of which are overgrown with oysters. He noted that many concretions are rolled and recorded bones of birds, ichthyosaurs, crocodiles and lizards. He states 'the dark phosphatic nodules usually named coprolites'. No name could be more unfortunate, for there is no evidence of their coprolitic origin; the only coprolites found, those of small fishes, are among the rarest fossils of the bed.

Chalk Rock Member, Upper Chalk Group

Phosphate occurs as hardgrounds in the Chalk Rock Member, which occurs at the base of the Upper Chalk in eastern and southern England. In the Hitchin area the main phosphatic horizon is at the top of the Chalk Rock (Hopson *et al*., 1996). The hardground was described as a highly convolute surface mineralised by both calcium phosphate and glauconite, and both the surface and the underlying bed of chalk stone are penetrated by thalassinoid burrows. The surface is overlain by a bed of indurated chalk containing glauconitised and phosphatic pebbles, which also yields superbly preserved mineralised internal moulds of original aragonite shelled molluscs (notably ammonites), an association previously noted from older strata. They concluded (on p. 54) that mineralised hardgrounds developed on the contemporary sea floor during breaks in sedimentation.

Neogene
Coralline Crag

The Coralline Crag comprises shallow-marine, shell-detrital sediments that are thought to be of late Pliocene age (Sumbler, 1996). The formation has a small outcrop near Aldeburgh, Suffolk, and contains three phosphate pebble beds. The basal bed was first excavated for fertilizer in 1820, but the phosphate industry developed from 1846 with the discovery of superphosphate (Ford and O'Connor, 2009), and peaked locally in 1857. It has been described as a 'remanié bed' (Boswell, 1927) and as a 'basal conglomerate lag deposit' (Balson, 1999). Its phosphate and calcareous mudstone pebbles were derived from the London Clay, whereas large flint pebbles, quartz, igneous rocks, bones and teeth came from older rocks. Rare in the Crag gravel are cobbles of Suffolk Boxstone, a muddy and slightly glauconitic sandstone with phosphatic cement, commonly enclosing casts of fossils. These are thought to have been derived from Neogene strata that are no longer preserved.

Red Crag

This formation rests unconformably on the Coralline Crag and comprises high-energy, shallow-marine shelly sands. A discontinuous conglomerate, widely exploited for phosphate, occurs at or near the base. Phosphate pebbles also occur in discontinuous layers and are scattered at higher levels. The basal bed, the Suffolk Bone Bed contains phosphatic mudstone pebbles derived from the London Clay, some of which contain crab and lobster remains. Shark and ray teeth are associated with rolled bones of walrus, cetaceans

Figure 12. Phosphatic fossils from the Cambridge Greensand.

Figure 13. Phosphatic fossils from the Pleistocene Red Crag.

and the terrestrial mammal Mastodon (Fig. 13). Other pebbles include Suffolk Boxstone, Coralline Crag, flints, Jurassic limestone, quartz and quartzite with Mesozoic fossils including belemnites (Balson, 1999).

Conclusion

The phosphate in these Mesozoic and Cainozoic deposits generally occurs as either authigenic (*in situ*) nodules or as allogenic (derived) pebbles. Many of the latter comprise reworked nodules and phosphatised animal remains, particularly ammonites. Small amounts of derived phosphatic bones, fish teeth and scales may occur at the base of major discontinuities. A unique feature is provided by the phosphatic pisoliths in the Whitby Formation. The rarity of coprolites is notable, and it is recommended that future use of this term is restricted to confirmed fossil faeces.

An equally valid view is expressed by Ford and O'Connor (2002) in their description of coprolite mining that was a major industry in the latter half of the 19th century. The term coprolite was then applied to all phosphatic material whatever its origin. Having quoted the Oxford English Dictionary definition of coprolite (a stony roundish fossil consisting of, or supposed to consist of, the petrified excrement of an animal), they extend the usage to include phosphatic nodules. Purists might wish to refer to the latter by terms such as pseudo-coprolites, or false coprolites for those that cannot be shown to be excretions. The debate continues.

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