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FOSSILISATION PROCESSES IN TERRESTRIAL ENVIRONMENTS AND THEIR IMPACT ON ARCHAEOLOGICAL DEPOSITS

Lucy M. E. McCobb

A dissertation submitted to the University of Bristol in accordance with the requirements of the degree of Doctor of Philosophy in the Department of Earth Sciences, Faculty of Science.

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Declaration

The work contained in this thesis is the author's own, except where stated or referenced accordingly. The views expressed in this thesis are those of the author and do not represent those of the University of Bristol.

Lucy McCobb

Lucy M. E. McCobb

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CHAPTER 1. INTRODUCTION

1. 1. Introduction and aims

This thesis explores the processes and conditions involved in the preservation of biological materials in terrestrial archaeological deposits, with two main objectives. The first is to gain a better understanding of how and why the biological raw materials of archaeology (principally seeds, fruits, bones and arthropod remains) become fossilised and to assess what inaccuracies may be introduced to archaeoenvironmental reconstructions as a result of preservational biases. The second objective is a much wider one: to determine what preservational information from archaeological deposits can reveal about fossilisation in general and in more ancient settings.

The main processes that transform organic material during decay and early diagenesis are selective decay of certain biomolecules (and hence, selective concentration of others), conversion of biomolecules to more recalcitrant (decay-resistant) forms, and replacement of volatile (readily decayed) tissues with authigenic minerals (Allison, 1988a). Archaeological material may make a valuable contribution to our knowledge of these processes, none of which is fully understood at present. Fossilisation pathways may be reconstructed more easily and reliably by studying relatively young (sub-) fossil material and progressively moving to older material, than by merely looking at the start (modern) and end (ancient fossil) points of the preservation continuum.

The investigation of biomolecule preservation is a relatively new and rapidly growing area. In general, structures composed of resistant biomolecules may survive for millions of years to become

incorporated into the fossil record, whilst those which lack these biomolecules decay rapidly. However, in reality there is much variation in biomolecule behaviour, between tissues, species and depositional settings. Study of archaeological material may elucidate some of the complexities of biomolecule preservation by demonstrating the early effects of diagenetic processes in different settings.

It has recently been demonstrated that laboratory experiments can contribute significantly to our knowledge of fossilisation processes and their associated biases. Sub-fossil archaeological material represents a level of preservation intermediate between specimens decayed or mineralised experimentally, over a period of several months, and those preserved in the ancient fossil record, millions of years old. Information gained about the preservational processes operating in archaeological deposits may be used to address taphonomic problems in the ancient fossil record. For example, characteristic abundance or absence of a particular species in the fossil record may be explained by its selective survival or decay during early burial and diagenesis, trends which will already be apparent in late Quaternary deposits.

Despite the obvious potential, with the exception of archaeological bone, there have been virtually no taphonomic studies of sub-fossil material from archaeological deposits to date. The broad aims of this study are to elucidate the processes by which organisms become preserved (or not) in terrestrial archaeological deposits, and to identify the associated biases. Within this broad area, a number of specific problems will be addressed. For example, some archaeological deposits yield exclusively waterlogged organic remains, whilst others are dominated by mineralised material.

Between these two extremes are deposits which preserve a mixture of organic and mineralised fossils, and both types of preservation sometimes even occur within the same fossil. These two preservation regimes may be associated with distinct species, or different tissues within the same species, depending on structural or compositional differences.

The same broad approach is applied to all of the archaeological specimens analysed. The quality of structural preservation and associated chemical composition is determined, principally using SEM, electron microprobe/EDX (composition of mineralised tissues) and flash pyrolysis-gas chromatography/mass spectrometry (composition of non-mineralised tissues). Such data are sparse for modern species so, where possible, extant examples of the same species are analysed for comparative purposes. Hence, the preservational pathways associated with different deposits are reconstructed and predictions made as to which species have the highest preservation potential in those settings, based on their chemical composition and structural characteristics.

The results of this research may also make a valuable contribution to improving the protocol for the treatment and storage of archaeological biological materials. Degradation processes may be initiated or continue once a specimen is removed from the ground, so knowledge of the parameters controlling these processes can be applied in conservation. There is an increasing trend towards conserving archaeological materials by leaving them in the ground, within their natural depositional setting. However, if this policy is to ensure the long-term survival of fossils and artefacts, then careful consideration must be given to the treatment of sites following re-burial of archaeological sediments. For example, addition of

limestone to an acidic, peaty site may alter the groundwater pH to the extent that degradation of any biological materials present is accelerated (Hall, *pers comm.* 1999).

Before exploring what archaeological deposits can reveal about fossilisation in terrestrial environments, the nature of the terrestrial fossil record is reviewed, ranging from deposits millions of years old up to more recent, archaeological settings. The range of organisms known to be preserved in different depositional settings provides a useful starting point from which to explore the range of terrestrial fossilisation regimes. Research to date on the processes of decay and fossilisation is also summarised below, as a platform on which to build hypothetical pathways to explain the preservation of archaeological remains in specific settings. The principles behind the main practical techniques employed are included in the introduction, although specific treatments of individual samples and additional analyses are also covered in the relevant chapters.

1. 2. The terrestrial fossil record

1. 2. 1. Ancient deposits

1. 2. 1. 1. Animal fossils

The fossil record is dominated by the hard or biomineralised parts of marine animals. The fossil record of terrestrial organisms is more sparse and is dominated by bones and shells which have found their way into water bodies. Non-shelly terrestrial invertebrates, which often lack mineralised tissues, may also be preserved in water-lain deposits under exceptional circumstances.

However, fossilisation in truly terrestrial environments is very rare. This is in part due to the lack of biomineralised tissues in the majority of invertebrates, which decay rapidly upon death. Their

chances of survival may be increased by rapid burial, which inhibits scavenging and promotes anoxia, but this is improbable in the absence of water-borne sediment.

The few autochthonous terrestrial fossil deposits include coals, mineralised peats and amber, although the last is often reworked. Research into the terrestrialisation of arthropods has relied almost exclusively on the extraction of organic cuticle fragments from macerated rock and mineral samples, principally Carboniferous coals (see Francis, 1961; Goodarzi, 1984; Bartram et al., 1987).

The Lower Devonian (Siegenian) Rhynie Chert of Scotland represents an unusual set of terrestrial preservational conditions (Selden & Edwards, 1989). Terrestrial arthropods (mites, collembolans and trigonotarbids; extinct, close relatives of spiders) were preserved amongst *in situ* vegetation by the rapid precipitation of silica, thought to be associated with the eruptive phases of a hot spring complex.

The Joggins deposit (Westphalian B, Carboniferous), Nova Scotia preserves terrestrial arthropods and small vertebrates, found within *Calamites* and *Sigillaria* stumps (Carroll, 1970). Extensive flooding in the Carboniferous forested Joggins area resulted in breaking off of vegetation at ground level. The resulting stumps were buried in subsequent sediment layers and rotted internally, forming natural pitfall traps. The trapped arthropod fauna includes arthropleurids, millipedes and a scorpion (Briggs *et al.*, 1979).

Amber represents an important mode of preservation in terrestrial settings, particularly for our knowledge of fossil insects. Although fossil resins are known as early as the Carboniferous, notable amber faunas are only recovered from Cretaceous and younger deposits, corresponding to the start of significant resin production. The

Palaeogene Baltic (Larsson, 1978) and Dominican Republic (McAlpine and Martin, 1969) ambers are the most famous of hundreds of localities known worldwide (see Langenheim, 1990; Dietrich, 1975; McAlpine and Martin, 1969). Amber faunas are restricted to small organisms, principally insects, other arthropods and plant remains, which became trapped in resin exuded onto tree surfaces. Very rare small vertebrates may also be recovered (Poinar, 1988). Hardening of the resins via cross-linking and isomerisation processes conferred stability and degradation resistance to the amber (Mills *et al.*, 1984), which may be recovered from accumulations in marine settings or *in situ*, e. g. from coal seams (Dietrich, 1975).

1. 2. 1. 2. Plant fossils

The majority of terrestrial plant fossils are recovered from lacustrine or marine sediments following transport in air or water, making it difficult to reconstruct their original habitat and ecology (Greenwood, 1991). These problems are exacerbated by the continual shedding of leaves, seeds and other reproductive structures throughout a plant's life, so that it may potentially produce a number of different fossils. Furthermore, each type of plant organ displays different transport characteristics, resulting in a tendency for different components of an individual plant to be preserved in a number of disparate deposits.

Autochthonous plant assemblages may be preserved by peatification. Peat forms when the sub-soil and humic layers become waterlogged and anoxic, retarding decay processes and allowing the long-term accumulation of plant matter (see **1. 3. 3.** preservation of biomacromolecules). Peat macrofossil assemblages are usually dominated by seeds and fruits, root systems, stems and woody axes

derived from the peat-forming plant assemblage. Fossilised peat is abundant in the form of Mesozoic and Cenozoic coal seams, but its highly altered state means that specific plant material is usually unrecognisable.

Rarely, silicification of peat may take place. The classic example is the Rhynie Chert of Aberdeenshire (see above), which preserves peat interspersed with plants in growth position (Selden & Edwards, 1989). Seeds, blossoms and other plant structures may be recovered from amber (see above).

1. 2. 2. Quaternary deposits

The majority of fossilisation processes in truly terrestrial settings result only in ephemeral preservation; hence, the fossils that they produce are restricted to Quaternary deposits. Although archaeological deposits are Quaternary in age, they are dealt with separately from "natural" deposits, in a later section of this thesis, so that the affects of man's activities on their taphonomy can also be considered. Peat, amber (see above), asphalt, permafrost, salt deposits and dry caves all represent natural environments where microbial activity, and hence decay, may be inhibited.

A number of asphalt deposits are known throughout the world, the most famous being the Californian tar pits which include the Pleistocene Rancho La Brea. These pits range from 6 000 to 32 000 years BP and are renowned for their vertebrate fauna which includes sabre-toothed cats and wolves (Marcus & Berger, 1984; Van Valkenburgh & Hertel, 1993; Van Valkenburgh, 1994; Duckler & Van Valkenburgh, 1998). However, a range of insect taxa have also been recovered, possibly attracted to the tar by carrion, by its water-like appearance or by properties of the tar itself (Stock, 1992). Although

most of the specimens recovered from asphalt deposits consist of bones and teeth, some soft tissues are preserved at Rancho La Brea, including chitinous insect cuticle (Stankiewicz *et al.*, 1997c) and the tracheal rings of birds.

Entire mammoths and bison have been discovered in the Pleistocene glacial permafrost of Siberia (Kurten, 1986; Guthrie, 1990). These preserve skin, hair and some muscle but have usually decomposed internally, creating a body cavity. Insect fossils have also been recovered from the dung of a frozen mammoth carcass (Elias, 1992).

The importance of packrat middens as a source of arthropod sub-fossils has only recently been appreciated, with studies of middens from the Sonoran Desert of Mexico, ranging in age from modern to 9 970 years BP (van Devender & Hall, 1993). Taphonomic studies have been limited to biostratinomic considerations of the provenance of the species preserved and their mode of transport into the middens. The taphonomic importance of faecal deposits in general has yet to be explored.

A Pleistocene swamp in Galicia, Poland yielded a number of "pickled" mammals, including a woolly rhinoceros (Niezabitowski, 1911). The carcasses were permeated with salt and oil and preserved in three dimensions, with hair and skin intact.

Ritualistic mummification of human cadavers by the ancient Egyptians is well known, but the precursor of this process was the natural mummification of cadavers by desiccation in arid conditions. For example, desiccated ground sloths have been recovered from South American desert caves (Cartelle & Deluliis, 1995; Hoss *et al.*, 1996) and naturally mummified human cadavers survived over 5000 years in Egyptian tombs (Brothwell, 1987).

With the exception of amber and asphalt, the preservation media discussed above provide only a temporary barrier against microbial processes; removal of a carcass from its matrix initiates decay. Survival of carcasses over geologically significant periods of time usually involves either authigenic mineralisation (replacement of soft tissues by minerals), survival of soft tissues due to the presence of decay-resistant biomolecules, or the conversion of constituent biomolecules to a more recalcitrant form.

For example, three-dimensional millipedes recovered from a late Pleistocene/Holocene cave deposit preserve delicate structures, including limbs and eyes, through mineralisation in calcite (Donovan and Veltkamp, 1994). This mode of preservation is attributed to the originally high calcite content of the millipede cuticle, which may have acted as a nucleus for further deposition from calcium carbonate-rich ground water. Louis Leakey (Leakey, 1952; Lees, 1953; Leakey, 1963) made reference to three-dimensional calcified millipedes and beetles from the Miocene Rusinga beds of Lake Victoria but the taphonomy of these arthropods has never been considered.

1. 2. 3. Archaeological deposits

Although they date from the same geological period, archaeological deposits are considered separately from other Quaternary deposits, as the activities of man may produce unique depositional environments and demand the consideration of additional, anthropogenic, taphonomic factors.

1. 2. 3. 1. Arthropods

Organic arthropod remains

In waterlogged archaeological settings, the recalcitrant sclerotised elytra of Coleoptera (beetles) tend to dominate arthropod assemblages, although cuticles of the Diptera, Hymenoptera and Hemiptera are also commonly recovered, in addition to spiders and mites. Cuticles of the other insect orders are rare. The other major groups of terrestrial arthropods, the Isopoda (woodlice), Diplopoda (millipedes) and Chilopoda (centipedes) rarely survive under these conditions, except where their cuticles are protected by concretions of diagenetic minerals.

Mineralised arthropod remains

While the organic cuticles of woodlice, millipedes and centipedes are rare in archaeological deposits, these arthropods have reputedly been recovered from a number of deposits as calcium carbonate casts (Girling, 1979). Non-mineralised insect cuticles may be recovered from the same deposits, in addition to calcified insects, of which dipterous puparia are most common. Rare calcified beetles also occur (Girling, 1979), and Girling (1984) has reported an adult and a nymph human louse, a pubic louse and a bedbug nymph from a late 17th/early 18th century horn-core lined pit at Cutler's Garden, London. Calcification of arthropods is typically associated with organic-rich pits and drains in hard water areas, which are regularly flushed with calcium carbonate-saturated water. The apparent taxonomic bias associated with calcification (towards woodlice, millipedes and centipedes) is attributed to differences in cuticle composition (Girling, 1984). The Isopoda, Diplopoda and Chilopoda strengthen the cuticle via impregnation with calcium carbonate

during development, and lack a well-developed waxy cuticle to prevent water loss. It is thought that these factors combine to enhance the probability of calcite precipitation on or within decaying carcasses.

Similarly, arthropods replaced by calcium phosphate have been recorded from organic-rich deposits such as Potterne, a Late Bronze Age midden in Wiltshire (Carruthers, 2000). Indeed, Girling (1979) states that in the "calcified" dipterous pupae that she studied from other deposits, levels of P are significantly higher than in the soil from which they were recovered, with substantial increases in iron also recorded. This suggests that these fossils were actually replaced by calcium phosphate, rather than calcium carbonate; it is not clear what the "simple analyses" used by Girling and colleagues (1979) to establish the elemental concentrations actually were, and whether they were sufficient to distinguish between these two authigenic minerals.

1. 2. 3. 2. Plants

The plant macrofossils recovered from archaeological deposits (principally wood, seeds and fruits) are typically carbonised (charred) or associated with waterlogged sediments. In aerobic sediments, uncarbonised plant remains only survive where desiccation or mineralisation has taken place, or as impressions in ancient pottery or tufa (Körber-Grohne, 1991).

Charred plant remains

The plant parts found as charred or carbonised remains in archaeological deposits are restricted to seeds, fruits, stems, tubers, buds, wood and cereal ears, glumes, and rachis fragments (Körber-

Grohne, 1991). This very biased range, compared with other preservational categories, is due to the direct relationship between this mode of preservation and the crop processing techniques employed by our ancestors. Despite an extremely limited taxonomic range, charred plant remains are extremely valuable because they occur in many more archaeological sites than plants preserved in other ways, extending our knowledge of human diet in Europe back into the early Neolithic, where other plant remains are rare. This is because the preservation of plants as charred remains is less dependent on sediment type than their preservation in other modes. Plant remains have also been recovered from charred peat and animal dung, in areas where wood was scarce and these were used as fuel.

Waterlogged plant remains

Preservation of organic plant remains in waterlogged archaeological settings has yielded the widest range of plant parts and taxa. In addition to seeds and fruits, various parts of cereal grains (glumes, rachis parts, awns and testa fragments), capsule segments, pods, flower parts, stems, stalks, rhizomes, roots and leaves have all been recovered from archaeological deposits in a waterlogged state (Körber-Grohne, 1991). There appears to be some taxonomic variation in the quality of preservation of seed coats in waterlogged deposits, e. g. Leguminosae with soft seed coats and large fruited Umbelliferae tend to be poorly preserved (Körber-Grohne, 1991). Deposits yielding waterlogged remains include pits, wells, dwelling and burial mounds, lake-shore and coastal settlement layers, and peat bogs.

Desiccated plant remains

The desiccated plant remains so far recorded from archaeological sites comprise vegetative plant parts, flowers, seeds, fruits, glumes and fruiting inflorescences (Körber-Grohne, 1991). The completely dry conditions required for this style of preservation mean that in the Old World it is generally restricted to caves, graves and other sheltered sites in areas such as the Mediterranean, Near East and Egypt. There is a vast literature on dried plant remains recovered from Egyptian burials, dating back as far as the First Dynastic age (3500-3000 BC, e. g. Helbaek, 1953). Four outstandingly preserved opium poppy heads were also found in a comparably-aged Neolithic cave burial in the Province of Granada, Spain (Neuweiler, 1935). More rarely, dried plant remains have been recovered from houses, e. g. chaff fragments within the clay of Bronze Age (approximately 3500 to 1000 BC) sun-dried bricks from Dendra, Greece (Hjelmqvist, 1977), and straw and threshing remains in the woodwork between storeys, and within the daub in the walls of 14th to 18th century houses in Germany (Willerding, 1987). In addition to plant remains, desiccated items fashioned from botanical raw materials have been found. For example, Egyptian graves have yielded cloth from the Dynastic and later Periods (3500 BC onwards), and cord, nets, baskets and wickerwork have been recovered from sites such as a Neolithic (3500 to 3001 BC) cave at Nahal Hemar in the desert near the Dead Sea in Israel (Korber-Grohne, 1991).

Much of the research so far carried out into the preservation of biomolecules in ancient plants has targeted desert sites, based on the assumption that arid conditions inhibit microbial activity, and that fossils from these sites have been subjected only to chemical degradation processes. Much of this work has focused on desiccated

material recovered from 1400 year old storage jars at Qasr Ibrim, Upper Egypt. Investigations of DNA preservation in material from this site are discussed in **3. 3. 1.** van Bergen *et al.* (1997) studied the composition of desiccated barley kernels and radish seeds from Qasr Ibrim, demonstrating only minor degradation and no obvious distinctions from fossils deposited under aquatic conditions. Evershed *et al.* (1997) reported further work on this material which provides evidence for the Maillard reaction during the decay of organic matter. Volatiles released during maceration of the material included alkyl pyrazines and alkyl polysulphides, known by-products of the degradation of amino acids and sugars by the Maillard reaction. Browning of the fossil seed tissues is attributed to the heteropolymeric products of the reaction.

Mineralised plant remains

It is likely that mineralised remains have often been overlooked in the past due to the standard techniques employed by environmental archaeologists during processing of archaeological sediments for site reports. These generally comprised flotation methods aimed specifically at recovering light carbonised remains. Denser mineralised specimens are usually detected only where sediments are sieved and the residue examined microscopically, a procedure which is now commonly included in archaeological sediment processing.

Körber-Grohne (1991) recognised two different categories of inorganic compound commonly associated with mineralisation; metallic compounds and salts, i. e. early diagenetic minerals. Replacement of plant remains by metallic compounds is relatively rare and typically occurs through precipitation of the corrosion products of adjacent metal artefacts, particularly those of iron (e.g. see

Keepax, 1975) and bronze. This special style of preservation has very little impact on the fossil assemblages studied by environmental archaeologists.

Preservation of biological remains in early diagenetic minerals is less directly dependent on human activity. The minerals typically involved, including carbonates and calcium phosphate, are common products of naturally occurring processes, and thus the fossilisation processes also occur in non-anthropogenic deposits. Körber-Grohne (1991) cited seeds cast in potash (potassium hydroxide) as the most frequently encountered mineralised plant remains but other minerals have also been reported, including gypsum (Helbaek, 1969), calcium carbonate (Dimbleby, 1978) and calcium phosphate, which is the most common mineral that occurs in British deposits (Green, 1979).

Helbaek (1969) described "calceous-gypseous" plant remains from Tepe Sabz, an ancient (5500 to 5000 B.C.) village sequence from the Deh Luran Plain, Khuzistan, Iran. Poorly preserved carbonised remains were coated in heavy gypseous or calcareous deposits, making identification highly problematic. This style of preservation is attributed to precipitation from salt-rich irrigation waters. However, where remains have not first been carbonised, calcareous pore waters may be conducive to a high quality of preservation, as exemplified by mineralised plant remains recovered from a food storage pit on the same site. The plants, preserved as calcareous-gypseous casts, included shell-less almonds, linseeds, caper seeds, grasses, seeds of an indeterminate cruciferous plant, large reed fragments and several other unidentifiable fragments. Preservational quality ranged from apparently perfect replication of two entire linseeds, including epidermal cells, to unidentifiable mineralised

fragments. Helbaek (1969) suggested that the extent to which a given species is mineralised is determined by the permeability of the seed coat: semi-permeable integuments allow internal mineral deposition during fluctuations in the ground water level.

1. 2. 3. 3. Vertebrates

The majority of vertebrate remains recovered from archaeological deposits are bones, ranging from isolated, poorly preserved fragments to complete skeletons. Whilst much attention concentrates on hominid remains, the bones of other mammals, birds, fish and reptiles are also recovered, and these have important palaeoenvironmental implications, as well as revealing details of past human diet. Hominid remains are often recovered from graves, and different funereal practices such as post-mortem delay before burial, coffining, cremation and defleshing clearly have an important impact on the likelihood of skeletal survival.

In some cases, the bones have dissolved away completely, leaving an external mould in the sediment which can be infilled with latex to reconstruct the original skeleton (Martill, 1991). Silhouettes or pseudomorphs of human skeletons are also known (e. g. from Sutton Hoo; Bethell & Carver, 1987), where the dissolved bones have been replaced by a dark brown loam, in two or three dimensions. This mode of preservation is not fully understood but it is postulated that breakdown products of phosphorus and collagen (peptides and amino acids) are adsorbed to soil colloids, where they form organo-metallic complexes with manganese and other biophile elements in the soil (Bethell & Carver, 1987).

While the persistence of vertebrate soft tissues far back into the fossil record is rare, even relatively short term preservation is

important in holding skeletons together long enough for their intact inclusion in sedimentary deposits. Mummification usually implies preservation of soft tissues to some extent and is associated with extreme environmental conditions where decay is impeded. Freezing temperatures inhibit bacterial activity and result in freeze-drying, depriving putrefiers of essential water. Desiccation may also occur in hot, dry conditions or in high concentrations of mineral salts (see **1. 2. 2.** for examples).

Fossilised red blood cells have been reported from human bones buried on the Island of Failaka in the northern Persian Gulf, dating from the Hellenistic Period (330-150 BC) (Maat, 1991; Maat, 1993). Although the burial conditions associated with the bones were considered, the exact nature and mechanism of mineralisation was never investigated.

Forensic studies of exhumed human cadavers have revealed the importance of adipocere in soft tissue preservation (Mant, 1987). Adipocere is a mixture of fatty acids formed by saponification, a post-mortem process involving hydrolysis and hydrogenation of body fats. The adipocere draws water out of the body's internal tissues, resulting in their preservation by mummification. Evershed (1992) investigated the composition of adipocere within a bog body from Meenybradden, County Donegal, using thin layer chromatography, gas chromatography, gas chromatography/mass spectrometry and microanalytical chemical transformations. The adipocere comprised fatty carboxylic acids, and the absence of intact triacylglycerols, diacylglycerols and monoacylglycerols indicated that complete hydrolysis had taken place. The decay pathway proposed for adipocere formation involved ester hydrolysis, ß-oxidation and reduction, in agreement with previous studies on adipocere.

"Lindow Man" (Stead *et al.*, 1986) and "Tollund Man" (Glob, 1969) are two of the best known among hundreds of human cadavers which have been recovered from the bogs of Northern Europe. These "bog bodies" often preserve skin, hair and internal organs but bones rarely survive the acidic bog waters. Soft tissue preservation is a result of tanning of collagen by the polysaccharide sphagnan (Painter, 1991). Sphagnan and other peat constituents indirectly limit microbial activity by sequestering essential metal cations. However, despite popular belief to the contrary, it is unlikely that peat contains an anti-microbial agent, or that low pH and anoxia are sufficient to halt microbial processes (Painter, 1991).

Little is known about the taphonomy of non-mammalian vertebrates in archaeological contexts but a few studies have concentrated on differences in the distribution of different skeletal elements between natural and human accumulations (e.g. see Colley, 1990 for fish, and Livingston, 1989 for birds). Different methods of butchering, cooking and eating carcasses can result in distinctive patterns of bones, and the actions of scavengers and carnivores associated with human settlements (such as dogs and rats) must also be considered.

1. 3. Processes

1. 3. 1. Decay

Decay is the usual fate of dead organic material, as decomposers recycle nutrients in the biosphere. If soft-bodied organisms in particular are to survive long enough to become fossilised, decay must be halted or at least retarded. The rate of decay of a carcass is dependent on a number of factors, principally supply of oxidants,

characteristics of the sedimentary setting and nature of the organic carbon being degraded (Allison, 1990).

Up until relatively recently, there was a popular misconception that anoxia prevents decay but experimental decay of invertebrates in both aerobic and anaerobic settings (Plotnick, 1986; Allison, 1988a, 1990; Kidwell & Baumiller, 1990) has shown that anaerobic decay may be rapid. Where oxygen is available, carcasses are rapidly degraded by aerobic microbial respiration. However, over 600 cm^3 of oxygen is required for every 1 g of organic carbon, so oxygen depletion is common and the majority of decay is actually anaerobic (Allison, 1988a). The size of the carcass is an important factor as the increase in mass/surface area ratio with size will inhibit diffusion, although the critical carcass size will vary with temperature and other factors (see below).

In the absence of oxygen, bacteria employ alternative electron acceptors. An ideal sediment profile may be envisaged, where different microbial communities consume different oxidants in an ordered fashion. Managanese, having the greatest free energy yield after oxygen, is consumed first, near the oxic/anoxic boundary (see Figure 1. 1.). Depletion of manganese is followed by reduction of nitrates, iron and sulphates, with a decrease in free-energy yield moving down the profile. When all of these have been consumed, methanogenesis (or carbonate reduction) takes place, with the consumption of CO_2. Fermentation, a respiration process involving neither oxidation nor reduction, may occur throughout the sediment profile but is mainly associated with the area below the carbonate reduction zone due to its low free energy yield (Allison, 1988a).

	AEROBIC	$CH_2O + O_2 + CO_2 + H_2O$
ANAEROBIC	Nitrate reduction	$5CH_2O + 4NO_3^- \rightarrow 2N_2 + 4HCO_3^- + CO_2 + 3H_2O$
	Manganese reduction	$CH_2O + 3CO_2 + H_2O + 2MnO_2 \rightarrow 2Mn^{++} + 4HCO_3^-$
	Iron reduction	$CH_2O + 7CO_2 + 4Fe(OH)_3 \rightarrow 4Fe^{++} + 8HCO_3 + 3H_2O$
	Sulphate reduction	$2CH_2O + SO_4^{--} \rightarrow H_2S + 2HCO_3^-$
	Methanogenesis	$2CH_2O \rightarrow CH_4 + CO_2$

Figure 1. 1. Idealised profile, showing the dominant microbial decay pathways in sediments, going from highest (AEROBIC) to lowest (Methanogenesis) free energy yield.

In practice, these oxidants may occur on a highly localised scale so that a number of different anaerobic decay reactions may occur simultaneously within a small area of otherwise dominantly aerobic sediment. The availability of oxidants is also variable so that sulphate reduction and methanogenesis dominate anaerobic decay in marine environments, methanogenesis and nitrate reduction in freshwater settings (Allison, 1990).

It has been suggested that decay may be slowed down in anaerobic settings because there is a lower free energy yield than that from aerobic respiration, which supports a greater diversity of bacteria (Berner, 1981). However, the evidence for this is equivocal and it is estimated that, at best, anoxia reduces the decay rate by one order of magnitude (Cannfield, 1989). It is clear that anoxia alone cannot halt decay but it may promote the survival of articulated carcasses by inhibiting scavenging and bioturbation (Allison & Briggs, 1991). The availability of oxidants will clearly depend on features of the sediment such as chemistry, porosity and permeabiltiy. Other

characteristics of the sediment, such as temperature and pH, also affect the decay rate.

Temperature is an important control on the rates of activity of both microbes and the enzymes that they produce. Bacteria have optimum temperature ranges, outside of which they are retarded or killed. The rate of enzyme-catalysed reactions increases with temperature, with an approximate doubling of decay rate achieved for every 10°C increase, until a critical temperature is reached where permanent structural damage occurs and enzymes are denatured (Allison & Briggs, 1991).

The majority of microbes function best at neutral or near neutral pH, and microbial activity is restricted in highly acidic or alkaline conditions. The classic example is peat bogs where tannic and fulvic acids in pore waters limit the microbiota which can survive. However, preservation of human cadavers in peat is attributed to tanning of the skin by sphagnan, a polysaccharide, rather than simply to reduced microbial activity (Painter, 1991).

Organic carbon occurs in many different forms, combined with other elements, principally nitrogen, oxygen and phosphorus, in molecules of varying resistance (Eglinton & Logan, 1991). Tissues with relatively decay resistant macromolecules of organic carbon are known as refractories, as opposed to labiles which usually decay readily. Refractories often have a structural or protective role in life, for example arthropod cuticles. Hence, when an arthropod decays, for example, the muscles usually decay rapidly but the chitinous cuticle persists for longer. Enclosure within biomineralised structures, such as collagen in bones, may also confer increased decay resistance on macromolecules.

Ironically, the ions released during anaerobic decay processes are essential for early diagenetic mineralisation of carcasses. Hence, exceptional preservation of soft tissues involves a delicate balance between decay and mineralisation; some decay is essential but too much will leave nothing to preserve (Allison, 1988a).

1. 3. 2. Authigenic mineralisation

Decay of soft tissues occurs rapidly, even in anaerobic environments, so mineralisation must occur very early in diagenesis if they are to be fossilized. Authigenic mineralisation most commonly involves carbonates, pyrite, and phosphates, although pyritised remains have never been recovered from terrestrial archaeological deposits.

1. 3. 2. 1. Carbonates

Exceptional preservation of soft tissues more commonly involves carbonates than any other minerals. Fossilisation in carbonates may involve the formation of nodules or concretions, where the carbonate is concentrated around an organism. The other main type of ancient carbonate deposit is the *Plattenkalk*; these fine-grained, well- bedded limestones (Allison, 1990) are known from a number of sites around the world, including the famous Jurassic Solnhofen Limestones of Bavaria (Barthel *et al.*, 1990). *Plattenkalks* may yield exceptionally well preserved fossils, but since their formation is associated with stratified water columns in marine settings, they have limited application to terrestrial archaeological deposits.

Carbonate formation is intimately associated with anaerobic decay processes. The most common pathways, involving reduction of iron, sulphate, nitrate or manganese, all produce bicarbonate ions which

may combine with cations to form carbonates. The most common forms are calcite (calcium carbonate) and siderite (iron carbonate). The mineral which forms is determined by the dominant decay pathway. In freshwater settings, which are most applicable to terrestrial archaeological deposits, sulphide ions are virtually absent and iron ions may exceed those of calcium, allowing siderite to form (Allison, 1988a). In marine settings, iron ions combine preferentially with the sulphide ions produced by sulphate reduction, forming pyrite, and sea water is usually supersaturated with calcium, so that calcite is the most likely carbonate species to form.

Various models proposed for the formation of carbonate concretions involve reaction with the bicarbonate ions released from the carcass itself (Berner, 1968; Raiswell, 1976). However, although bicarbonate ions may be produced around a decaying organism, the carcass alone is unlikely to produce sufficient ions to form a nodule. It is likely that the carcass acts as a precipitation sink for bicarbonate ions produced during the decay of disseminated organic material in the sediment (Allison, 1990).

An explanation for the presence of "coal balls" (carbonate concretions representing permineralised peat) within Upper Carboniferous coal seams remains problematic. It is possible that the bicarbonate ions produced from the decay of organic matter in the peat became sufficiently concentrated to buffer the acidic pore waters and allow carbonate formation. However, the presence of marine bands overlying the coal seams is strongly suggestive of marine influence (Scott & Rex, 1985), an idea supported by the stable carbon isotope values of the coal ball calcites, which indicate both marine and freshwater sources (Scott *et al.*, 1996).

1. 3. 2. 2. Pyrite

Pyrite is a common component of fine-grained marine clastic sediments and its formation is closely linked with anaerobic decay. Hydrogen sulphide, produced by sulphate-reducing bacteria, may combine with reactive iron-bearing minerals to form iron monosulphides (FeS) such as mackinawite and greigite. These may react further with sulphur, liberated by microbial breakdown of hydrogen sulphide, to form pyrite (FeS_2). Hence, the main requirements for pyritisation are organic carbon (a food supply for the bacteria), dissolved sulphate and detrital iron minerals (Berner & Raiswell, 1984). Sulphate is relatively rare in freshwater systems so pyritisation is much more probable in marine environments (Allison, 1988a). The absence of sulphate probably also explains why pyritised remains have never been reported in terrestrial archaeological deposits.

1. 3. 2. 3. Phosphates

Calcium phosphate ($Ca_5(PO_4, CO_3)(OH, F, Cl)$) is probably the most commonly occurring mineral in archaeological deposits. It forms very early in diagenesis, so that it results in the highest fidelity of soft tissue preservation of all of the diagenetic minerals. Three-dimensional phosphatised fossils are known from a number of localities throughout the world, including the Upper Cambrian Orsten of southern Sweden, where tiny arthropods are preserved in spectacular detail within calcitic concretions (Müller, 1985). Phosphatisation is limited to the cuticle of arthropods of 2 mm or less and the phosphate source is unclear. Larger concretions from the Lower Cretaceous Santana Formation of Brazil yield fabulous fish in which muscle fibres are preserved down to the level of cell nuclei

and striations, and gills are present with arteries, veins and secondary lamellae intact (Martill, 1989). Comparison with experimentally decayed trout indicated that phosphatisation must have occurred less than five hours after death, although the reliability of this work is questionable as it was carried out on separate chunks of muscle rather than whole fish. The time taken for decay of complete carcasses is likely to be significantly longer, at least days rather than hours.

It is not yet clear why apatite should form so early in diagenesis. Normally, concentrations of bicarbonate ions produced during anaerobic decay far exceed those of phosphate ions so calcite is preferentially precipitated in carcasses (Allison, 1988a). This has been visualised as a calcium carbonate-calcium phosphate "switch", with the default position set for $CaCO_3$ precipitation. For phosphatisation to occur, pore water phosphate ions must reach a concentration which exceeds that of bicarbonate ions. One suggested phosphate concentration mechanism involves adsorption of phosphates released by decay to ferric hydroxides in the sediment (Benmore *et al.*, 1983). With the onset of anoxia, reduction of ferric iron would release phosphates into pore waters near the anoxic-oxic boundary, creating a phosphate concentration peak.

Laboratory experiments on invertebrates (e. g. Briggs & Kear, 1994a & b) have revealed the effects of decay-induced pH changes on mineralisation. "Open" conditions allow the acidic by-products of microbial metabolism (e. g. CO_2 and H_2S) to escape, so alkaline conditions persist and calcium carbonate precipitation takes place. In "closed" (anoxic) conditions, the acidic by-products accumulate, leading to a fall in pH which favours apatite precipitation. These effects may operate on a highly localised scale, with phosphatised tissues and calcite crystal bundles occurring in different areas of the

same carcass. Their distribution may reflect varying phosphate concentrations in different tissues of the body or the effect of the cuticle "envelope" in maintaining high ion concentrations and low pH (Briggs & Wilby, 1996).

Furthermore, the "switch" is dynamic. In some decay specimens, apatite precipitation was followed by $CaCO_3$ precipitation, associated with a gradual rise in pH after initial decay (Briggs & Kear, 1994a). Examples of this can be seen in the fossil record, e. g. *Mesolimulus* specimens from Solnhofen preserve $CaCO_3$ crystal bundles enclosing phosphatised muscle tissue (Briggs & Wilby, 1996). The calcite overgrowths may have an important role in protecting the phosphatised tissues from damage.

1. 3. 3. Preservation of biomolecules

Many organisms lack mineralised tissues in life, so that their fossilisation is dependent on either authigenic mineralisation or the survival of decay-resistant organic material. Non-biomineralised tissues vary in their susceptibility to decay, ranging from labile tissues such as muscle, which will survive only through rapid authigenic mineralisation, to more recalcitrant tissues (known as refractories), which may survive relatively unaltered as organic fossils.

The fossil record of plants relies heavily on the survival of refractory tissues and organs, principally leaf cuticles, pollen and spores, seed coats, fruit walls, periderm, wood and resins (van Bergen *et al.*, 1995). These owe their preferential survival to the presence of resistant biomacromolecules, and typically have a structural or protective role during life. Organic preservation is less prevalent in the zoological fossil record but it is particularly important for our

knowledge of the arthropods (e. g. see Butterfield, 1990) and graptolites (e. g. see Briggs *et al.*, 1995a).

Biomolecules are universally present in extant organisms but exhibit a great variation in their resistance to decay and behaviour during diagenesis (Eglinton and Logan, 1991). In addition, the same macromolecule may behave differently depending on a number of factors. The physical location of the macromolecule, both on a gross scale (e. g. whether it is disseminated throughout the tissue or localised within a storage organ) and on a molecular scale, will affect its susceptibility to degradation. Also, where two or more biomolecules form a complex (such as lignin and cellulose), the preservation potential of the individual biomolecules is usually enhanced. Since decay is microbially mediated, any characteristic of the depositional environment which restricts microbial activity (see **1. 3. 1.**) will enhance the chances of biomolecule survival. Although a great number of variables affect how long a particular biomolecule will survive, a spectrum of relative decay resistance can be recognised, based on the maximum timescale of survival of the various biomolecules. This section begins by reviewing the chemical structure and preservation potential of the major groups of biomolecule, which are dealt with in order of approximate increasing decay resistance (nucleic acids, proteins and tannins; the carbohydrates hemicelluloses, cellulose and chitin; lipids and the "resistant biopolymers", comprising lignins, cutins, suberins, cutans, suberans and sporopollenins). Although research into some of these biomolecules has focused exclusively on their survival in deposits of substantial geological, rather than archaeological age, they are included on the principle that if they persist in some appreciably older fossils, then they may play an important role in the

preservation of archaeological remains. This is followed by a summary of the research into fossilisation of the three major categories of organic remains (propagules, wood and arthropod cuticles) that are commonly recovered from archaeological (and in some cases, significantly older) deposits.

1. 3. 3. 1. The principal biomolecules

Nucleic acids

DNA (deoxyribonucleic acid) and RNA (ribonucleic acid) are the carriers of genetic information in all living cells (de Leeuw & Largeau, 1993) They consist of chains of sugars (deoxyribose and ribose, respectively), joined together via phosphate ester links, and with purine (adenine and guanine) or pyrimidine (cytosine, uracil and thymine) bases attached at the 1' position (Figure 1. 2.)

Figure 1. 2. Generalised structure of a nucleic acid.

Nucleic acids have a generally low preservation potential outside living cells. They are susceptible to fragmentation via hydrolysis of phosphate links, although this may be prevented in tissues which are

rapidly desiccated after death (e. g. see Pääbo, 1993 for studies of DNA in mummies and other ancient museum specimens). Even dried specimens are susceptible to oxidative damage, which may result in loss of or damage to pyrimidine bases or sugars (Eglinton and Logan, 1991). The preservation potential of DNA may be enhanced if it is enclosed within a protective matrix, for example within bone tissue (Pääbo, 1993).

The advent of PCR meant that even tiny fragments of DNA could be amplified to give recognisable sequences, although contamination from modern sources is a serious problem. Claims were made for extraction of DNA from a number of extinct mammals, including a 40 000 year old frozen woolly mammoth, and initial results suggested that survival in even more ancient specimens might be possible. A DNA sequence of a 17 million year old magnolia leaf from Clarkia, a lacustrine deposit, was published by Golenberg and colleagues in 1990, although subsequent attempts to extract DNA from other leaves from the site proved unsuccessful, detecting only contaminant bacterial DNA (Sidow *et al.*, 1991).

Amber insects have been widely acclaimed as the most promising source of ancient DNA, with reports of DNA from 40 million year old specimens; two independent laboratories claimed to have succeeded in isolating DNA from six or more specimens (see Stankiewicz *et al.*, 1998). However, when the degradation of DNA was investigated and it was established that it is unlikely to survive beyond 10 000 years (Lindahl, 1993), major doubts were cast on previous claims of DNA preservation. Subsequent attempts to extract DNA from amber of various ages have failed (Austin *et al.*, 1997; Walden & Robertson, 1997).

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Despite the absence of DNA in deposits of geological age (see Briggs *et al.*, 1999 for review), archaeological applications of preserved DNA sequences have been possible (e. g. Krings *et al.*, 1997). Exceptional circumstances, such as very arid conditions, are necessary to allow the persistence of DNA even for a few centuries. For example, O'Donoghue *et al.* (1994) provided the first unequivocal evidence for the presence of the three pyrimidine bases (cytosine, uracil and thymine) and two purine bases (guanine and adenine) of DNA and RNA in desiccated radish and barley seeds from 1400 year old storage jars at Qasr Ibrim, Upper Egypt, using gas chromatography/mass spectrometry with selected ion monitoring (GC/MS-SIM) data and gas chromatography/tandem mass spectrometry (GC/MS/MS) product-ion spectra, and liquid chromatography/mass spectrometry with selected ion monitoring (LC/MS-SIM) with electrospray ionisation (O'Donoghue *et al.*, 1996a). Previous studies of ancient seeds reported the presence of ancient DNA in charred wheat (Allaby *et al.*, 1994) and maize (Goloubinoff *et al.*, 1993), and in desiccated maize and cress (Rollo *et al.*, 1991). Polymerase chain reaction (PCR) of the Qasr Ibrim radish DNA confirmed its taxonomic identity, illustrating the potential importance of ancient DNA in the identification of problematic archaeobotanic material.

Proteins

Proteins occur universally as the most abundant constituents of cells (De Leeuw and Largeau, 1993). They consist of polypeptides which are chains of amino acids joined by peptide bonds (Figure 1. 3.)

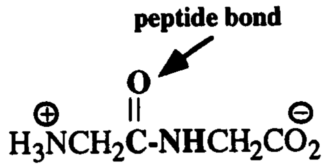


Figure 1. 3. Generalised structure of a dipeptide, comprising two amino acids linked by a peptide bond (indicated in bold).

An enormous variety of proteins exists, arising from different combinations of twenty common amino acids. Proteins have many different functions, acting as catalysts (enzymes) and regulators (e. g. insulin), and in transport, storage, defence and structural roles (de Leeuw and Largeau, 1993). There are two broad categories of proteins, globular and fibrous, arising from differences in their tertiary structure, i. e. the manner in which polypeptide chains associate with each other. Globular proteins consist of polypeptide chains which are tightly folded together via hydrogen bonding, cross linking, dipolar interactions and interactions with water molecules (Eglinton and Logan, 1991). These proteins have hydrophilic amino acids on the outside, and are consequently water soluble. The tight folding of the polypeptide chains may confer some protection from degradation to interior amino acids. Globular proteins include enzymes, antibodies and nutrient storage proteins.

Fibrous proteins are long, stringy, insoluble molecules which usually have structural or protective roles (Eglinton & Logan, 1991). They often have a quaternary structure, whereby protein fibres are tightly bound together via hydrogen bonding and cross linking. For example, collagen consists of a triple helix of protein chains which, in addition to enclosure within a mineral matrix (bone), is thought to confer increased resistance to degradation.

In general, however, proteins are easily degraded to their constituent amino acids which may then be used in cellular metabolism. Polypeptide chains are broken down via hydrolysis of peptide links by proteolytic exoenzymes and peptidases, and side chain functionalities may also be attacked. Proteins typically hydrolyse to their constituent amino acids within 100 000 to 1 million years (Bada *et al.*, 1999), so that they are not usually preserved in deposits of geological age. However, proteins *are* commonly preserved in archaeological materials, where they have a variety of applications. Proteins that have suffered only partial degradation have been recovered from 1400 year old desiccated plant material from Qasr Ibrim (Bland *et al.*, 1998) but, despite the successful application of immunological techniques to the detection of structurally recognisable proteins (Tuross & Stathoplos, 1993), sequencing of proteins from archaeological remains has not proved fruitful (Lowenstein & Scheuenstuhl, 1991). Fortunately, the main uses of proteins in archaeological material do not require the preservation of intact protein sequences (Briggs *et al.*, 2000). The isotopic signal of collagen and other proteins present in archaeological material may provide information on palaeodiet (e. g. see Pate, 1994; Pollard, 1998; Macko *et al.*, 1999) and may also be used for radiocarbon dating. Flannery *et al.* (1999) used HPLC (high performance liquid chromatography), flash pyrolysis-GC/MS and SEM to establish that collagen is exceptionally well preserved in the skin of ancient human bog bodies and mummies, with very similar amino acid distributions to modern human skin.

Tannins

Tannins are polyphenolic compounds capable of precipitating proteins from aqueous solutions, found in the cell walls of higher plants and some algae (de Leeuw & Largeau, 1993). They are divided into three groups: the condensed tannins or proanthocyanidin polymers (PAC), the phlorotannins (PT) and the hydrolysable tannins (HT).

PAC are probably universally present in the major gymnosperm groups and widespread among the woody angiosperms (de Leeuw & Largeau, 1993). They are rare or possibly absent in non-woody angiosperms. Structurally, they are non-lignin polyphenols, composed of polyhydroxy flavan-3-ol units linked via C-C bonds, and they are resistant to hydrolysis by acids and bases. There is a great variety in PAC structure, which is affected by a number of different features (see de Leeuw & Largeau, 1993 for details). In all PAC-containing tissues, the bulk of PAC are glycosidically bound to a carbohydrate matrix such as cell wall "hemicellulose". PAC are usually found together with lignins in woody plants (although see van Bergen et al., 1997a) and they form major constituents of barks in numerous species. They also dominate in the leaves of some cotton species.

Figure 1. 4. A flavan unit, which forms the structural basis of PAC. R = H or CH_3.

Tannins exhibit antimicrobial properties because they are able to interact with proteins, so various PAC have broad antimicrobial spectra. Tannins have also been noted to accumulate in dead or dying cells, so they would intuitively be expected to contribute substantially to fossil organic matter.

Attempts to hydrolyse soluble PAC resulted in formation of an insoluble material via further polymerisation, and this chemical stability in hydrolysing conditions increases with initial degree of PAC polymerisation (Goodwin & Mercer, 1972). Hence, a high preservation potential would be anticipated for PAC. However, although PAC might be predicted to have a high preservation potential, the fact that they are non-hydrolysable means that they are not often detected in fossil material. One of the few records of tannins in ancient material is a report of their presence in fossil bark in brown coals (Wilson & Hatcher, 1988).

Phlorotannins (PT) have been detected only in brown macroalgae so they are not considered further here.

Hydrolysable tannins (HT; see de Leeuw and Largeau, 1993 for structure) may be found in the cell walls of almost any plant organ,

although the highest HT concentrations have been recorded in seed pods. Along with PAC, they are considered important for structural rigidity. HT can be degraded by a large number of esterases and their chemical stability is relatively poor, so that their preservation potential is relatively low.

Hemicelluloses

Hemicelluloses are polysaccharides closely associated with cellulose in vascular plant cell walls. Three of the principal hemicelluloses are xylans, mannans and galactans (de Leeuw & Largeau, 1993).

Xylans are very widespread and abundant in vascular plants and consist of (1->4)-linked β-D-xylose units (Fig. 1. 5.).

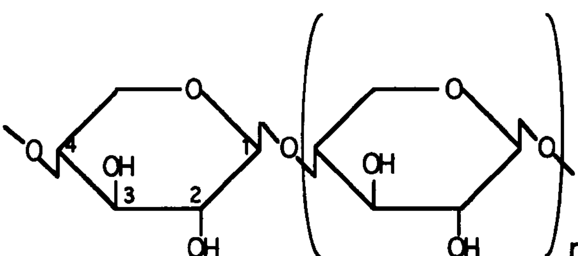


Figure 1. 5. The structure of xylans, comprising a chain of (1->4)-linked β-D-xylose units.

Other sugars may also be present as side chains e.g. (1->3)-linked α-L-arabinose. Xylans have a much lower molecular weight than cellulose and are much more rapidly degraded.

Mannans may occur as homopolysaccharides or as constituents of heteropolysaccharides. They consist of linear chains of (1->4)-linked β-D-mannose, with side chains of α-D-galactose (attached via (1->6)

linkages) present to varying extents depending on the species (Figure 1. 6.).

Figure 1. 6. The structure of mannans, comprising chains of (1->4)-linked β-D-mannose, with side chains of α-D-galactose (attached via (1->6) linkages).

Various mannans are present in hardwood, including D-gluco-D-mannan which consists of β–D-glucose and β–D-mannose units (1->4)-linked in linear chains. In coniferous wood, D-gluco-D-mannans occur with α-D-galactose units (1->6)-linked as a side chain.

Galactans are water-soluble, highly branched polysaccharides. The backbone chain consists of (1->3/6)-linked β–D-galactose units, and a variety of side chains are present via (1->6) linkages, e. g. L-arabinose and L-rhamnose.

Cellulose

Cellulose is the most abundant biomacromolecule in nature, occurring principally in the cell walls of woody higher plant tissues but also in algae and lower plants (de Leeuw & Largeau, 1993). It is a

linear homopolysaccharide, consisting of 10 000 or more (1 -> 4)-linked β-D-glucose units (Figure 1. 7.)

Figure 1. 7. The structure of cellulose, comprising a chain of (1 -> 4) linked β-D-glucose units.

The glucose chains are cross-linked to each other via numerous hydrogen bonds, creating insoluble fibrils.

Cellulose may be degraded by fungi and Eubacteria under aerobic conditions and by specific groups of bacteria anaerobically, yielding low-molecular weight fatty acids such as acetic acid and propionic acid (de Leeuw & Largeau, 1993). However, cellulose is preserved to a certain extent in Recent and ancient sediments, probably due to the formation of complexes with lignins. Pyrolysis products of cellulose have been detected in Miocene water soldier seed coats (van Bergen *et al.*, 1994a, 1995), wood (Lücke *et al.*, 1999) and a leaf vein from Clarkia (Logan, 1992), as well as in Oligocene fruits (Boon *et al*, 1989) and Eocene wood (Spiker & Hatcher, 1987).

Chitin

Chitin is a homopolysaccharide, consisting of (1->4)-linked 2-acetamido-2-deoxy-β-D-glucose (Figure 1. 8.; Stankiewicz *et al.*, 1996).

Figure 1. 8. The structure of chitin, comprising (1->4)-linked 2-acetamido-2-deoxy-β-D-glucose.

Chitin is insoluble in water and many organic solvents (de Leeuw & Largeau, 1993). Chitin has a relatively high preservation potential and may be recovered from fossil insects back into the Tertiary, with the oldest chitin detected so far found in beetles from the 25 million year old lake deposits of Enspel, Germany (Stankiewicz *et al.*, 1997d).

Although most commonly associated with arthropod cuticles, chitin also occurs in the cell walls of fungi and certain green algae, and is typically complexed or covalently bound to other substances such as proteins (de Leeuw & Largeau, 1993). However, it can be degraded to its constituent monomers by a variety of bacteria, via enzymatic (chitinase and chitiobiase) hydrolysis.

Lipids

Lipids are defined as compounds that are soluble in organic solvents but insoluble in water, and include fats, waxes and phosphoglycerides (Streitwieser & Heathcock, 1985). They are synthesised by all organisms, principally as cell membrane constituents or for energy storage. Structurally, lipids include a wide variety of carbon skeletons, including linear and branched chains and

cyclic structures (Eglinton & Logan, 1991). Since most lipids are aliphatic, they have a low water solubility and hence, a high preservation potential. The hydrophobic nature of lipids also means that they are unlikely to undergo leaching in groundwater, allowing them to be easily related to their source material within sediments (Briggs *et al.*, 2000). However, once hydrolysed to their constituent fatty acids, lipids are more soluble and susceptible to microbial and chemical degradation. Lipids will be totally microbially degraded unless nutrients are limited or the depositional environment is hostile to bacteria. Inclusion within the protective matrix of archaeological seeds or bones may shield lipids from total degradation and in older deposits, sediment compaction may play a similar role. Arid conditions may also favour lipid survival, although autolytic hydrolysis may occur under these circumstances, as indicated by the presence of free fatty acids in desiccated seeds (O'Donoghue *et al.*, 1996b). Under favourable conditions, lipids may survive in an identifiable form for geologically significant periods of time.

Lipids recovered from fossils usually belong to one of two classes: *n*-alkyl lipids (straight chain compounds usually found as homologous series) and polyisoprenoids, which may be retained in their original form but are more commonly diagenetically altered (Briggs *et al.*, 2000). Lipids extracted from fossil material usually comprise a mixture of fossil-derived lipids, along with those contributed by degrading organisms. Bacterial contribution to the lipid signal may be identified by the presence of characteristic compounds, such as hopanoids.

Diagenetic changes to lipids are usually minor, e. g. loss of functional groups and hydrogenation of double bonds, and, as the carbon skeleton that is diagnostic in lipids, the structure of geolipids

can be used to infer that of the original biolipids (de Leeuw & Largeau, 1993). This is the basis of the lipid "biomarker" concept which allows characterisation of the depositional environment of organic-rich rocks, in terms of temperature and oxygen levels, as well as indicating the source material (e. g. higher plant, algal or bacterial).

Lipids are widely preserved in archaeological deposits, within bones (e.g. Stott *et al.*, 1996), plant remains, resins and tars, and within the porous fabric of potsherds (Evershed, 1993), and these are a valuable source of information on a variety of ancient human activities. Biomarkers for ancient manuring are provided by excreted sterol and bile-acid products from the mammalian gut (Evershed & Bethell, 1996; Bull *et al.*, 1999). The botanical ingredients of various ancient resins, tars and pitches have also been established using lipid biomarkers (e. g. Evershed *et al.*, 1997a; Mills *et al.*, 1994; Pollard & Heron, 1996). Evershed and Connelly (1988 & 1990) investigated lipid preservation in the muscle and skin of human "bog bodies", establishing that although fatty carboxylic acids and sterols were detected in both tissues, these were much more altered in the skin tissue. Cholesterol was very well preserved in the bog body muscle tissues. Isotopic measurements of archaeological lipids reveal information on their source compounds, as well as palaeodietary information. For example, the diagnostic $\partial^{13}C$ values for the $C_{16:0}$ and $C_{18:0}$ fatty acids of milk provided the earliest unequivocal evidence for dairying in prehistoric communities (Dudd & Evershed, 1998).

Fatty acids may also be recovered from Tertiary sediments, where the nature of their alteration indicates the maturity and thermal history of sediments (e. g. Huang *et al..*, 1996), but have yet to be identified in significantly older sediments (Briggs *et al.*, 2000).

Lignins

Lignins are high-molecular mass biopolymers which form an important constituent of vascular plant tissues (de Leeuw & Largeau, 1993). Highly heterogeneous, their structure varies between species and even between tissues of the same plant. The basic structure comprises phenylpropanoid units, which are variously oxygenated in the alkyl group and the benzene ring. This structure arises through dehydrogenative condensation of three monomers: ρ-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (Figure 1. 9.)

ρ-coumaryl alcohol | coniferyl alcohol | sinapyl alcohol

Figure 1. 9. The three basic monomers that undergo dehydrogenative condensation to form lignins.

The relative abundance of these "monolignols" determines the lignin structure. Gymnosperm (guaiacyl) lignins are derived mainly from coniferyl alcohol, whereas dicotyledonous angiosperm (guaiacyl-syringyl) lignins comprise both coniferyl and sinapyl alcohols. In addition, both of these lignin types have a low contribution from ρ-coumaryl alcohol. Monocotyledonous angiosperm lignins are dominated by coniferyl and ρ-coumaryl alcohols. Furthermore, the variation in lignin structure among

various monocotyledonous species suggests that there may be potential for chemosystematic analysis of lignins in fossil plant material (van Bergen *et al.*, 1994a, 1995).

Formation of lignins from monolignols occurs via an enzyme-initiated dehydrogenative polymerisation process (de Leeuw & Largeau, 1993). Dimers are formed within cells and their excretion is followed by radical polymerisation of dimers and monomers extracellularly. This occurs via random coupling of mesomeric phenoxy free radicals derived from monolignols (Figure 1. 10.).

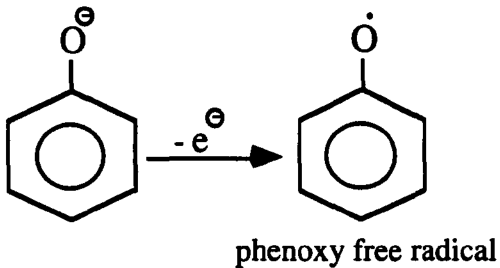


Figure 1. 10. Formation of phenoxy free radicals from monolignols.

Over ten phenylpropanoid linkages have been identified in lignins but alkyl-aryl ether bonds are dominant, in particular the β-O-4 type which accounts for 50 - 60% of linkages. Aryl-aryl and alkyl-alkyl carbon-to-carbon bonds are also present. Most linkages are head-to-tail but some head-to-head and tail-to-tail linkages are known. A three-dimensional structure is created by condensed units, where several linkages are formed with adjoining units. The terminal groups of the C_3 side chains are most commonly free alcohols but aldehydes occur in a few cases.

The stable, non-hydrolyzable ether and carbon-carbon bonds created during the final stages of lignin formation create insoluble

polymers which may be altered by oxidation reactions, whilst making complete degradation of lignins unlikely. Lignins are also relatively resistant to microbial degradation, being affected by a much narrower array of microbes than most other biopolymers. Fungi are the most efficient lignolytic organisms but their activities are restricted to highly aerobic settings. Although the exact mechanisms of lignin degradation are not fully understood, it is thought to mainly involve oxidation at double bonds along with demethoxylation or demethylation pathways (van Bergen *et al.*, 2000).

A relatively high chemical stability and resistance to microbial degradation mean that lignins are likely to survive early diagenesis, so that integral parts of lignin macromolecules may become incorporated into fossil organic matter. Hence, lignins are commonly preserved in archaeological remains and have also been detected in Miocene (Lücke *et al.*, 1999) and Eocene woods (Spiker & Hatcher, 1987), and Oligocene fruits (Boon *et al.*, 1989), in some specimens along with their associated cellulose.

Cutin

Cutin is present in the cuticular membranes that cover the external exposed surfaces of vascular plants, such as leaves, non-woody stems and fruits. It also occurs in some internal tissues such as inner seed coats. Its role is to protect the plant tissues against desiccation and microbial infection (de Leeuw & Largeau, 1993).

Structurally, cutin is a polyester composed of ω-hydroxy C_{16} and C_{18} fatty acids with various mid-chain functional groups (de Leeuw & Largeau, 1993). The latter are typically hydroxyl or epoxy groups, although epoxy groups may be limited to angiosperm cutins. There is considerable variation in fatty acid composition both between and

within plant species, at different developmental stages and/or in different environmental settings. There may also be a small amount of esterified phenolic acids in cutins.

The intramolecular structure of cutins is very poorly understood but it is thought that the primary hydroxyl groups are almost completely esterified, whereas most of the mid-chain hydroxyls are free (de Leeuw & Largeau, 1993). The unavailability of these free hydroxyls and other mid-chain groups for cross-linking means that cutins are essentially linear polyesters.

Cutins are easily degraded by fungi, using extracellular enzymes known as cutinases, and so are usually absent in fossil material. However, putative hydrolytic products of cutins have been detected in the Miocene sediments at Clarkia (Huang *et al.*, 1996).

Suberins

Suberins, like cutins, are macromolecular polyesters found in vascular plants (de Leeuw & Largeau, 1993). However, suberins are restricted to the woody tissues of plants, generally occurring as components of cork cell walls in periderm layers (both aerially and subaerially). They may also be found in some internal tissues, for example, the Casparian bands of the endodermis. Suberins play a similar protective role to cutins.

Studies of the chemical composition and structure of suberins are very limited but most of the suberin monomers identified to date are also known from cutins (de Leeuw & Largeau, 1993). Unique to suberins are monomers of greater length ($>C_{18}$) and with less mid-chain substitution. These longer monomers are mainly 1-alkanols and the corresponding fatty acids (C_{20}-C_{30}) and ω-hydroxy fatty acids (C_{16}-C_{24}), with a minor contribution from α, ω-diols. There may also

be a substantial contribution from esterified phenolic acids. The intramolecular structure of suberins is extremely poorly understood and only a tentative working hypothesis has been proposed.

Like cutins, suberins may be depolymerised by extracellular enzymes produced by fungi. However, although they do not usually survive in fossils, analyses using base hydrolysis have demonstrated their survival in some Recent sediments (Cranwell, 1991).

Cutans

Along with cutins, cutans make up the insoluble constituent of plant cuticles, the distinction between the two being that cutins are hydrolysable whereas cutans are not (de Leeuw & Largeau, 1993). Cutans are highly aliphatic and it has been suggested that they consist of cellulose fibres which are covalently bound to a polymethylenic sheath, thus protecting them from hydrolysis. Nonhydrolysable, insoluble aliphatic macromolecules were detected in the leaf and stem cuticles of various higher plants and in all fossil plant cuticles tested (Nip *et al.*, 1986a, b). Significantly, those modern plant cuticles thought to lack cutans are absent from the fossil record. Experimental treatment of cutans to simulate diagenesis and catagenesis resulted in the formation of *n*-alkanes commonly found in crude oils, suggesting that cutans are important contributors, and supporting the model of kerogen formation involving selective preservation of such resistant biopolymers (Tegelaar *et al.*, 1989).

However, more recent studies failed to find evidence to support the presence of cutans in any extant plant material analysed, suggesting that cutans actually represent diagenesis products found only in fossil material. One suggestion is that cutans arise from polymerisation reactions between aliphatic lipids, such as the waxes

that form a protective layer on the outer surface of cuticles (Mösle *et al.*, 1997; Collinson *et al.*, 1998; Stankiewicz *et al.*, 1998).

Suberans

Suberans are the equivalent of cutans in suberized plant tissues, i.e. nonhydrolysable polymethylenic macromolecules (de Leeuw & Largeau, 1993). The main difference is that suberans are partially soluble in organic solvents, suggesting less cross-linking than in cutans. Although suberans have so far been detected only in the bark of various higher plants (Tegelaar *et al.*, 1995), a similar compound has been discovered in the stem and root tissue of an Upper Carboniferous lycophyte (Collinson *et al.*, 1994). Suberans are thought to be the source of the coal maceral suberinite (Tegelaar et al., 1995), and may fulfill a similar role to lignins in strengthening plant tissues (van Bergen *et al.*, 1995).

Sporopollenins

The frequent occurrence in the fossil record of the outer walls (exines) of spores and pollen of vascular plants is attributed to the presence of resistant, nonhydrolysable macromolecules, known as sporopollenins. The precise chemical composition of sporopollenins remains unclear, although it is now known that carotenoids do not contribute as was originally thought (see van Bergen *et al.*, 1995). It is believed that there are two main types of sporopollenin, one derived from phenylpropanoid units and the other from long n-alkyl chains which may originate from fatty acids. Formation of sporopollenin is thought to involve external polymerisation, occurring at specific surfaces within the exines. Recently, Dominguez and colleagues (1999) claimed to have isolated purified sporopollenin from various

pollen species. The sporopollenin retained the original shape of the pollen grains. Fourier-transform infrared spectroscopy of the biopolymer revealed an absence of polysaccharide and phenolic compounds, and the presence of carboxylic acid groups joined to unsaturations and ether linkages. GC/MS analysis of the products of ozonolytic degradation of the putative sporopollenin revealed dicarboxylic acids with low numbers of carbon atoms, in addition to fatty acids and n-alkanes in some species.

Sporopollenins generally have a high chemical stability, although they are varyingly resistant to oxidation (de Leeuw and Largeau, 1993). The exines of some species disappear rapidly in oxic soils, for example, whilst others are apparently unaffected by microbial attack and chemical oxidation. For those species which are susceptible to oxidation, soil pH may have an important affect on decay rate, with better preservation observed under acidic conditions.

By virtue of the preservation potential of sporopollenins, exines may retain their full morphology in archaeological deposits and beyond, into the ancient fossil record, allowing species identification. Sporopollenins are believed to be precursors of the coal maceral sporinite (de Leeuw and Largeau, 1993).

1. 3. 2. 3. Studies of structures commonly preserved due to the presence of resistant biomacromolecules

Propagules (seeds and fruits)

In extant plants, the function of the resistant seed coat is to protect the underlying genetic material and food stores from mechanical, chemical and microbial damage so it is unsurprising that seeds (represented by their coats) may survive in substantial quantities to become preserved in the fossil record. The seed coat is typically made

up of the outer seed coat (the testa) and the inner seed coat (the tegmen). The testa is derived from the outer integument in the ovule, whereas the tegmen is derived from the inner integument. Testae tend to be sclerotic, the majority comprising lignin-cellulose or lignin-hemicelluloses as their insoluble constituent. Tegmens are often translucent in appearance and their insoluble fractions have a highly aliphatic composition similar to cutans (van Bergen *et al.*, 1994b).

Chemical studies of seed coats are rare to date. Those carried out on fossil material have exploited the fact that separation of the seed coat layers occurs during fossilisation, whereas they are very difficult to separate in extant material by mechanical or chemical treatment (van Bergen *et al.*, 1994a-c).

van Bergen *et al.* (1994a, b & c) carried out chemical and microscopic analyses of fossil (Eocene/Oligocene) and extant water lily (*Brasenia spinosa* and *Sabrenia chandlerae*) and water soldier (*Stratiotes cf. headonensis*) seed coats. The fossil samples were recovered from various lithologies but were otherwise comparable, having undergone similar burial histories. None of the seed coats showed visible evidence of biodegradation and microscopic studies revealed only minor morphological alterations, which were slightly more pronounced in seeds from coarse-grained sediments (van Bergen *et al.*, 1994c).

Regardless of the apparently high level of morphological preservation, all fossil testae had undergone some chemical alteration, indicated by the absence of specific carbohydrate (hemicelluloses and cellulose) pyrolysis products (van Bergen *et al*, 1994c). In some testae, all carbohydrate pyrolysates were absent and lignin had undergone major chemical alterations, producing a

relatively simple, highly cross-linked, polyphenol macromolecule. Degradation pathways leading to formation of such a macromolecule have been postulated for dicotyledonous and monocotyledonous lignins (van Bergen et al., 1994a):

Stages in lignin-cellulose transformation in dicotyledonous lignin:
(numbered points are in the approximate order in which they occur)

1) Slight relative decrease of carbohydrates (primarily due to loss of hemicelluloses). A minor increase of phenols and 1, 2 - benzenediols (due to oxidative alteration of methoxyphenols)

2) Carbohydrates (cellulose) completely removed.Dicotyledon lignin altered:

i) loss of 2, 6 - dimethoxyphenol units

ii) formation of 1, 2 - benzenediols moieties

iii) C3 side-chain degradation

iv) alkylation of the carbon atom next to the original ether linkage in lignin building units

v) a relative increase of alkylphenols

Stages in lignin-cellulose transformation in monocotyledonous lignin:

1) Removal of carbohydrates.

2) Loss of 4-hydroxybenzoic acid and related compounds, e. g. 4-hydroxybenzaldehyde and methyl 4-hydroxybenzoate.

3) Loss of 2, 6 - dimethoxyphenol units.

4) C3 side-chain degradation.

5) A dramatic increase of alkylphenols (other than phenol) relative to 2-methoxyphenols.

Despite apparent similarity in quality of morphological preservation between fossil testae from different lithologies, major differences in chemical preservation were noted, even amongst closely related specimens. Possible explanations for this include (van Bergen *et al.*, 1994c):

i) different autecology, resulting in preservation in different depositional settings;

ii) the native lignins had different compositions and therefore different susceptibility to similar diagenetic processes;

iii) chemical modification occurred prior to, or during, deposition;

iv) chemical modification occurred during reworking;

v) there were differences in the depositional setting such as presence/absence of inorganic compounds and/or clay minerals.

Chemical preservation of the insoluble constituents of water lily and water soldier testae was relatively better in coarse-grained than in fine-grained sediments (van Bergen *et al.*, 1994c). A possible explanation is that variation in grain size results in a variation in the amount of oxidation in the early stages of burial, organic matter being more readily oxidized in coarser grained material. The organic acids produced during oxidation would create an acidic environment, inhibiting microbial activity. In more clay-rich sediments, organic oxidation would be limited and the pH would remain more favourable for microbial life (and hence, degradation). Another possibility is that different inorganic constituents of the sediment, such as pyrite, influenced the quality of preservation.

Similar studies of the sclerotic seed coat of *Nymphaea caerulea* and the sclerotic propagule wall of *Nelumbo nucifera* (both water lilies) revealed the predicted presence of angiosperm lignin-cellulose in the

former (van Bergen *et al.*, 1997a). However, the fruit wall plus seed coat of *Nelumbo* is thought to be composed predominantly of polysaccharides and insoluble tannins (proanthocyanidins), that may form complexes with a similar structural role to lignin-celluloses.

A comparative study of modern and fossil (Upper Miocene) conifer cone scales and seeds revealed that the ligno-cellulose complex present in the seeds is more resistant to degradation than that in the scales (Stankiewicz *et al.*, 1997a), reflecting the different functions of these plant parts.

Ancient (ca. 1400 year old) barley kernels and radish seeds preserved by desiccation showed no visible evidence of morphological degradation, although chemical alteration was apparent (van Bergen *et al.*, 1997b). The ancient barley kernels, originally composed of a monocotyledon lignin-cellulose complex, showed a marked decrease in the abundance of polysaccharides and cinnamic acid moieties. Pyrolysis of the modern radish seed coat yielded mainly amino acid moieties (from seed coat proteins) but also a polyphenolic macromolecule and a small contribution from dicotyledon lignin-cellulose. This is the first discovered example of this unusual chemical composition in a modern, sclerotic plant tissue. This distinctive chemical composition was little altered in the ancient specimens.

Like seed coats, certain fruit endocarps may persist for geologically significant periods of time. For example, *Nyssa* (tupelo gum tree) endocarps from the late Oligocene Brandon lignite show a high degree of anatomical preservation (Boon *et al.*, 1989). However, pyrolytic comparison with modern endocarps reveals alteration of the original lignin-cellulose. Most of the carbohydrate material is

absent, although a small levoglucosan peak indicates the survival of some hexose residues.

A comparison between the composition of the endocarp and secondary xylem of *Nyssa* revealed significant differences in their lignin chemistry (Boon *et al.*, 1989). The endocarp is significantly enriched in guaiacyl-type lignin markers with an aliphatic side chain, relative to syringyl components, reflecting different degrees of oxygenation of the lignin. The less oxygenated and more aliphatic lignin in the fruit endocarps may contribute to their resistance to decay.

Wood

Historically, wood has been one of the organic structural materials most widely used by man, reflecting its properties of strength and relative decay resistance (Hedges, 1990). The structural properties of wood are related directly to its chemical composition, the bulk being composed of a small number of structural biopolymers. Some 95% of wood comprises cellulose, hemicelluloses and lignins. The remainder can be divided into organic substances such as fats and waxes, and inorganics, generally defined as the ash remaining after wood has been heated to 600°C.

The types and abundances of the biopolymers in wood varies between different cell types, between early and late wood and within individual cell walls, causing considerable variation in decay resistance (Hedges, 1990). The main decay agents of wood are fungi, principally the soft-rot, white-rot and brown-rot varieties. These fungi can degrade all chemical components of wood, although as obligate aerobes they are precluded by anaerobic conditions. Bacteria may function under these conditions, although their degradation rate

is much slower than that of fungi and they tend to utilise polysaccharides almost exclusively. Hence, lignins may preferentially survive in environments where oxygen is excluded, such as waterlogged soils.

A number of techniques have been employed to investigate the nature of degradation in ancient woods (solubility techniques, elemental analysis, isotopic analysis, nuclear magnetic resonance e. g. ^{13}C NMR, chemical degradation e. g. acid hydrolysis, CuO oxidation, analytical pyrolysis) and these have highlighted some general trends (Hedges, 1990). Firstly, soft (gymnosperm) woods tend to be more decay resistant than hard (angiosperm) woods (Hedges *et al.*, 1985). It is thought that this reflects differences in tissue structure and extractives content, rather than differences in biopolymer chemistry.

As discussed above, lignins tend to become concentrated relative to carbohydrates as degradation progresses. In addition, preferential degradation of syringyl relative to guaiacyl lignin units is observed in hard woods (Hedges *et al.*, 1985; Van der Heijden & Boon, 1994). This may be explained by the different anatomical location of these lignin units within the wood structure. Syringyl units are most common in the secondary cell walls, whereas guaiacyl units tend to be concentrated in the compound middle lamella (CML), sandwiched between secondary cell walls. Hence, the guaiacyl units would be protected from decay by a covering of degraded syringyl units. Significantly, pectin is also concentrated in the CML, which may explain its enhanced preservation relative to the other polysaccharides. In general, α-cellulose displays a greater resistance to degradation than hemicelluloses, although both disappear at similar rates in the early stages of peatification (van der Heijden & Boon, 1994).

In summary, resistance to degradation decreases in the following order:

guaiacyl & ρ-hydroxyl lignin structural units > syringyl lignin structural units > pectin > α-cellulose > hemicelluloses (Hedges *et al.*, 1985).

Arthropod Cuticles

Arthropod cuticles are renowned for their decay resistance as they are known throughout the fossil record, from the Cambrian to the present-day. They are typically composed of microfibrils of the biopolymer chitin, covalently cross-linked to a protein and lipid matrix via catechol-amine and histidine/aspartic moieties (Figure 1. 11; Stankiewicz *et al* ., 1996):

Protein
HN
N
Catechol
OH
H_2COH
O
O
O
Chitin
OH
H_2C
CH_2
C=O
R
NH
C=O
CH_3
n

Figure 1. 11. Chemical composition of the arthropod cuticle, comprising chitin cross-linked to a protein and lipid matrix via a catechol-amine moietie.

The relatively common occurrence of arthropod cuticles in the fossil record has led to a long-held assumption of chitin survival. However, studies claiming to have found evidence of chitin preservation in cuticles as far back as the Cambrian (Carlisle, 1964) have failed to find support in more recent analyses (Rolfe, 1962; Voss-Foucart & Jeuniaux, 1972; Schimmelmann *et al.*, 1988; Baas *et al.*, 1995).

Analytical pyrolysis (py-GC/MS) of laboratory decayed shrimp cuticle revealed selective survival of chitin over proteinaceous components (Baas *et al.*, 1995). However, pyrolytic analyses (py-GC and py-GC/MS) of a range of Palaeozoic and Mesozoic cuticles failed to yield any pyrolysates which were directly attributable to either chitin or proteins (Stankiewicz *et al.*, 1997b). Instead, cuticle pyrolysates were either highly aliphatic or highly aromatic. The diagenetic pathways leading to these products are not clear. The aliphatic signatures may arise from the polymerisation of waxes and/or lipids from the cuticle surface or internal tissues, but the formation of the aromatic products remains enigmatic. Laboratory thermal maturation experiments have successfully simulated the transformation of arthropod cuticle to give these highly diagenetically altered chemical signatures (Stankiewicz *et al.*, 2000).

However, chitin *has* been detected in Cenozoic fossils. Small amounts of amino sugars present in the calcified skeletons of Cretaceous and Tertiary decapod crustaceans were considered indicative of chitin (Brumioul & Voss-Foucart, 1977), and Miller and colleagues (1993) used an enzymatic technique to detect significant quantities of chitin in Quaternary beetles. More recently, py-GC/MS has been used to detect the presence of chitin in insect sub-fossils from the Pleistocene asphalt deposits of California (Stankiewicz *et al.*,

1997c) and in 25 million-year-old fossil insects from the Oligocene Enspel lacustrine shale in Germany (Stankiewicz *et al.*, 1997d).

Chemical characterisation of invertebrate cuticles using py-GC and py-GC/MS allowed identification of potential markers for each of the major cuticular components (Stankiewicz *et al.*, 1996). Acetylpyridones, acetamidofuran, 3-acetamido-5-methylfuran and 3-acetamido-(2 and 4)-pyrones have been proposed as chemical markers for the presence of chitin. Markers for the proteins and catecholamine and histidine linkages present in cuticles have also been proposed (see Stankiewicz *et al.*, 1996). Quantitative data on the preservation of chitin in various modern, decayed and fossil arthropods were obtained using a colorimetric assay (Bierstedt *et al.*, 1998). However, this technique has its limitations when applied to fossil material, so ideally it should be combined with a qualitative technique, such as py-GC/MS.

1. 3. 4. Bone fossilisation

Factors affecting bone preservation

Skeletal completeness is very important in ancient population studies that rely on identification of individuals, so human taphonomic studies tend to concentrate on the decay and preservation of bone (Henderson, 1987). Deposition of vertebrate carcasses in a sediment body is usually essential for fossilisation, and this typically involves transport in rivers or other water bodies (Lyman, 1996). Aeolian deposition may also occur, whereby sediment or the carcass itself is transported by wind. Rarely, the bones of fossorial animals dying of natural causes in their burrows may be preserved *in situ*. Other terrestrial depositional settings include the various natural "traps" (bogs, marshes, springs and tar pits) discussed

in Section 1. 2. 2.. Death by entrapment is followed by sinking of the carcass into the associated sediment.

Intrinsic properties of bones, including size, shape, age and density, affect the decomposition rate to some extent but characteristics of the burial environment are more influential (Henderson, 1987). Water is vital for organic decay, and may also have a leaching effect on mineralised tissues so that bone (and overall carcass) preservation is better in relatively dry, well-drained soils than in deeper, waterlogged surroundings. Mummification of complete cadavers may occur in both hot (e. g. see Brothwell, 1987) and freezing (e. g. see Guthrie, 1990) arid settings, although the recovery of complete skeletons is still dependent on bone survival.

Soil type is also an important factor: acidic soils (including peat) promote dissolution of the mineral matrix of bones and those with a high salt content have a similarly destructive effect (Henderson, 1987). Hence, bone preservation is usually best in neutral or moderately alkaline soils. Temperature, and hence latitude, season and depth of burial, are important controls on the decomposition rate. Increasing the temperature accelerates the rate of chemical reactions. Carcasses decay much more rapidly, for example, in the tropics than in temperate regions during the winter.

The presence of oxygen has important implications for the decay rate of soft tissues but anoxia may also indirectly enhance the preservation of skeletons by retarding the decay of connective tissues long enough for fossilisation of entire, articulated skeletons. The porosity and density of soils clearly influence the amount of oxygen present.

Flora and fauna of all sizes may affect the preservation of bones. Mammalian carnivores and scavengers may actively disarticulate and

transport carcasses, breaking individual bones, and they may disturb buried bones through their activities. Other creatures are also important in subsurface contexts; insects and snails may disturb carcasses indirectly by burrowing and some species actively seek out and attack decaying cadavers. Bacteria and fungi attack the organic fraction of bone and roots may cause significant bone destruction in densely vegetated areas.

Bone diagenesis

The bulk of vertebrate bone is composed of calcium hydroxy apatite ($Ca_{10}(PO_4)_6.2OH$), the remaining twenty or so percent of its weight made up of proteins, principally collagen (Hedges *et al.*, 1995). Diagenetic alteration of the mineral portion of bone is often limited to ionic substitutions between OH and F or Cl, and between PO_4 and CO_3 (Martill, 1991), but in more extreme cases dissolution can occur, in addition to recrystallisation or overgrowth of bones by cryptocrystalline calcium phosphate. Characteristics of the burial environment, in particular the hydrological regime in operation, the groundwater composition (especially the concentration of calcium ions) and pH, are thought to be important in determining the rate of bone diagenesis (Hedges *et al.*, 1995). However, features of individual bones which increase their porosity (such as organic degradation and microbial attack) will clearly increase their susceptibility to the physical forces at work in the burial environment. Apatite may also be replaced by pyrite or other diagenetic minerals in some depositional environments. The pore spaces between the bone tissue frequently become infilled with a variety of diagenetic minerals, including pyrite, calcite and sphalerite.

Investigations of the preservation of the organic portion of vertebrate bone has focused mainly on collagen, the protein that accounts for ninety percent of the non-mineral fraction. Interest in collagen is in part due to its potential uses for dating ancient skeletons; ^{14}C dating can be carried out on the collagen itself (Bowman, 1990) or on its constituent small peptides or amino acids following hydrolysis and separation (van Klinken & Hedges, 1992). The extent of racemization of the individual amino acids is also being explored as a possible dating technique. There have been problems in applying this technique to collagen (Bada, 1991) but the more minor, robust proteins thought to be involved in the bone biomineralisation process show more promise (Ulrich *et al.*, 1987). The nitrogen $\partial^{15}N$ and carbon $\partial^{13}C$ isotopic composition of ancient collagen has also been explored as an indicator of palaeodiet (e. g. see Schwarcz, 1991). A number of immunochemical techniques have been applied to the detection of minor proteins in ancient bone, including osteocalcin, albumin and haemoglobin (see Childs & Pollard, 1992 for a review of this area). In addition to proteins, there have been successes in the recovery of other biomolecules from ancient bone. Several reports of PCR sequencing of DNA from ancient skeletons (e. g. see Hagelberg *et al.*, 1989) prompted concerns about modern contamination. However, a study by Richards *et al.* (1995) concluded that, although contamination is potentially a major problem when dealing with ancient human material, if necessary care is taken more than 50 % of skeletal remains from the past two thousand years are likely to yield amplifiable DNA. Evershed *et al.* (1995) succeeded in detecting the lipids remaining in ancient bone material.

Despite many studies focusing on bone collagen, the precise conditions and processes involved in its degradation remain elusive.

Collagen diagenesis is thought to be a two-stage process (see Collins *et al,* 1995): depolymerisation of the collagen by hydrolysis of its peptide bonds, followed by dissolution (or "melting free") of those resulting polypeptide fragments that are retained by fewer than a critical number of hydrogen bonds. However, the behaviour of collagen which is incorporated into a mineralised structure such as bone is thought to be more complex than that of "free" collagen because it is bound to the apatite (Lees, 1989). This is supported by experiments on collagen in bone, where the temperature at which it denatures and turns to gelatin is significantly higher than normal. The presence of hydroxyapatite clearly retards collagen diagenesis in some way. A mathematical model created by Collins *et al.* (1995) to explain the diagenesis of collagen in simple, non-biomineralised systems saw degradation being driven principally by hydrolysis of peptide bonds, a process which assumes the presence of an excess of water. In this case, collagen preservation would be enhanced by burial of bone in dry sites. Dehydration is also thought to increase hydrophobic interactions in collagen and strengthen existing inter-chain ionic linkages. The presence of the mineral matrix in bone is also thought to shield the organic molecules from degradation by physically excluding enzyme molecules, which are too large to penetrate it (Lees, 1989). Therefore, any burial conditions which lead to the dissolution of the hydroxyapatite, such as acidic soil, will enhance collagen degradation.

1. 4. The principal practical techniques employed

1. 4. 1. Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Analysis (EDX)

The equipment used for SEM and EDX analysis of the specimens discussed in this thesis was a Cambridge Instruments S250 Mk3 SEM, fitted with an Oxford Instruments PCXA energy dispersive X-ray analyser. As its name implies, SEM differs from light microscopy in that it uses a beam of electrons to illuminate specimens, rather than a beam of light (Chapman, 1986). The advantages of this technique over light microscopy are a much greater image resolution (typically down to 4 nm) and a greater depth of field (resulting in 3-D rather than flat images). Specimens can also be viewed from a wide range of angles, as the SEM allows movement in X, Y and Z-axes, as well as tilting and rotation.

The source of electrons in an SEM is a tungsten hairpin filament, which is heated to approximately 2300 degrees Celsius, the temperature at which it emits sufficient electrons to provide acceptable specimen illumination. The filament is heated until the "saturation point" is reached, i.e. the point at which an increase in temperature no longer brings about an increase in electron emission. In practice, this point is detected by watching a trace of the filament emission current on a cathode ray tube until an increase in temperature causes no alteration to the trace. The filament is housed within a cathode assembly, which has a high voltage applied to it, known as the "accelerating voltage". Typically between a few hundred and 40 000 volts, this is used to accelerate the emitted electrons down the electron-optical column. The higher the "accelerating voltage", the shorter the wavelength of the electron beam produced and the higher the speed of the electrons. A series of

electromagnetic lenses (consisting of wire coiled around an iron core) is used to focus the electron beam into a probe small enough to yield the required image resolution. Reflection coils direct the beam more or less along the lens axis. Each lens selects only those electrons forming the core of the beam, discarding those in the surrounding area, so that the beam gets successfully smaller in diameter as it passes down the column. The SEM is operated under a high vacuum to prevent disruption to the path of the electrons.

A number of different signal types are produced from specimens when they are hit by the electron beam. Electrons in the incident beam may cause inelastic scattering, i. e. they hit successive electrons within the specimen, knocking them out of their orbits and creating "free electrons" which may then leave the specimen as Secondary Electron (SE) emissions. Electrons from higher energy orbits typically fall down a level or more to fill the gap created, releasing the excess energy as X-rays. This process continues until the incident electron has expended all of its energy. Elastic scattering describes the situation where an incident electron passes near the nucleus of an atom in the specimen and is retarded by its electro-magnetic field, resulting in a change of direction and possibly a loss of energy (Bremsstrahlung Production). Rutherford scattered electrons (where energy is imparted to the specimen but little energy is lost from the incident electron) may be emitted from the specimen as Backscattered Electron Emissions (BEE), and may also be involved in inelastic scattering reactions, creating free electrons. The energy lost during both inelastic and elastic scattering reactions is emitted as X-rays, which are characteristic of the material in the specimen. This is the basis of Energy Dispersive X-ray Diffraction (or EDX) analysis, which can be used to assess the elemental composition of a specimen while

it is being studied under the SEM. The various signals produced by the specimen are collected by a detector, amplified and displayed on a cathode ray tube (CRT).

In preparation for examination under the SEM, specimens are typically mounted on aluminium stubs using Silver Dag adhesive and sputter-coated with gold; both of these processes ensure that the electron beam hitting the specimen is earthed. Where insufficient coating is applied, earthing may be prevented and the specimen may take on an electrical charge, obscuring the image.

1. 4. 2. GC/MS (Gas Chromatography/Mass Spectrometry), and Py-GC/MS (Flash Pyrolysis-GC/MS).

GC/MS (gas chromatography/mass spectrometry) combines separation of compounds using gas chromatography with their identification using mass spectrometry.

Gas chromatography partitions mixtures of solutes between two phases, the "mobile phase" and the "stationary phase" (Jennings, 1987). Separation is based on differences in vapour pressure (resulting in different "boiling points") and interactions with the "stationary phase". A basic gas chromatograph consists of a column (a capillary tube) within a thermostated oven. The stationary phase usually forms a thin film on the inner surface of the column. The column is continuously swept with the "mobile phase" (or carrier gas), which is typically helium.

Small quantities of the sample to be separated are introduced to the inlet end of the column, e. g. by injection as a dilute solution in a suitable organic solvent. Individual molecules of the solutes present vaporise, enter the mobile phase and are swept towards the detector in the carrier gas. Molecules are carried along in the mobile phase,

redissolve in the stationary phase further along the column and vaporise once more, this process continuing until a solute elutes from the end of the column. The proportion of each molecular species present in the mobile phase is a function of the solute vapour pressures. Solutes with higher vapour pressures (and lower "boiling points") enter the mobile phase more often and therefore make up a greater proportion of it. Solutes with lower vapour pressures (and higher "boiling points") enter the mobile phase less often, make up a lower proportion and hence take longer to elute at the detector end of the column.

Separation of different solutes therefore depends on differences in their volatility (i. e. "boiling point"), as this influences the rate of solute vaporisation and re-dissolution. It is these differences in rate that differentiate solute concentrations in the stationary and mobile phases. The most obvious means of altering solute vapour pressures is by adjusting the temperature of the GC oven. Gradually increasing the oven temperature will lead to the sequential vaporisation (and hence elution) of solutes of decreasing volatility. Vapour pressure may also be altered by using a different stationary phase, e. g. polar stationary phases reduce the volatility of polar solutes through additional interactions, such as hydrogen bonds.

Components eluting from the GC may be identified based on their retention times (the time taken from injection into the column to elution) or using MS (mass spectrometry). It is usual to employ a combination of identification techniques to increase the reliability of identifications. The combination of gas chromatography and mass spectrometry is particularly powerful, as the gas chromatograph supplies the mass spectrometer with one molecular species at a time, and the identification techniques employed (retention time and mass

spectral patterns) are based on entirely different molecular properties. A gas chromatogram consists of a relative abundance distribution of components plotted against their retention times.

Mass spectrometry is used to determine the structure of components after they have been separated by gas chromatography. Separated components are transferred to the ionising chamber of the mass spectrometer, where they are bombarded with electrons to form positively charged ions. The *molecular ion* consists of the intact molecule of a compound minus one electron, and this indicates the molecular weight of the compound:

$$M \xrightarrow{e^-} M^{+\bullet} + 2e^-$$

Molecular ions may fall apart during electron bombardment to form *fragment ions*, which in turn may fragment further. Fragment ions form through cleavage along specific lines of weakness in the molecule. Thus, there are characteristic fragment ions for every molecular ion that can be used to reconstruct the structure of the original molecule. The masses and relative abundances of the molecular and fragment ions produced are used to plot mass spectra, which display relative abundance against the mass to charge ratio (m/z). Since the charge for the molecular and fragment ions is normally +1, this is effectively a plot of relative abundance against mass. The fragment ion with the greatest abundance (highest peak on the spectrum) is known as the *base peak*. The molecular ion will clearly have a greater mass than its constituent fragment ions so it will plot furthest to the right on a mass spectrum. Combining gas chromatography with mass spectrometry involves identification of each peak on the gas chromatogram by plotting its mass spectrum.

The value of coupling pyrolysis with combined GC/MS lies in the insoluble nature of many complex macromolecules. Separation using gas chromatography clearly relies on the possession of some degree of volatility, rendering this an unsuitable technique for use on more inert macromolecules. However, pyrolysis (breaking bonds by heating samples in an inert or vacuous atmosphere) breaks macromolecules down into smaller molecular species, which are more volatile and amenable to separation and identification (see Boon, 1992; Irwin, 1993).

In practical terms, py-GC/MS involves introduction of the sample directly onto the heating filament or ferromagnetic wire (Curie-point pyrolysis) or (in the case of the work in this thesis) in a quartz holder placed within the wire coil.

For purposes of reproducibility, the conditions under which pyrolysis takes place must be tightly constrained (Irwin, 1993). The most important parameter to consider is, of course, temperature as it determines the pattern of macromolecule degradation. Hence, the pyrolysis (or equilibrium) temperature should be reached as rapidly as possible. In addition, the pyrolyser should be interfaced with the analyser to prevent escape of volatile pyrolysates. For py-GC/MS, pyrolysis is typically performed in a flow of helium (the carrier gas) so that volatile pyrolysates are swept directly into the gas chromatograph for separation. To ensure even heating of a sample, it should be as thin as possible, preferably less than 30nm.

An alternative to pyrolysis for rendering complex inert macromolecules suitable for GC/MS is chemolysis, a process of breaking bonds in the molecules by adding a chemical, usually involving hydrolysis by a strong acid or base. Following hydrolysis, the resulting small molecules are usually "capped off", to prevent

them from re-combining, by the addition of another chemical which attaches to the "open" bonds. The disadvantage of chemolytic techniques over pyrolysis is that they tend to target specific groups of compounds, e.g. proteins, whereas pyrolysis reveals the full range of biomolecules present. In addition, larger samples are usually required for chemolysis, whereas it is recommended that very small samples are used for pyrolysis, making it more suitable for relatively rare fossil material.

1. 4. 3. The role of experimentation

The application of experiments to palaeontology (aktuopaläontologie) is a natural progression from observational palaeontology, a long-standing approach based on the uniformitarian principle that observations of modern processes can be used to interpret those occurring in the past (see Briggs, 1995b). Experimentation has the advantage over observation in that variables can be controlled or simplified so that their individual roles in a given process can be monitored.

It has only recently been appreciated that experimental taphonomy can make a valuable contribution to palaeontology in a number of ways. Reliable interpretation of the fossil record, for studies of palaeoecology, diversity changes through time, etc., depends on identification of the biases introduced by taphonomic processes. It is important to be able to distinguish genuine absence from non-preservation and this can best be achieved through experimental study of decay processes. Organic decay has a central role in most fossilisation processes, including disarticulation and dissolution of skeletal material, biomolecule preservation and authigenic mineralisation of soft tissues. Hence, experimental decay is an

important approach to elucidating the conditions associated with fossilisation in different settings, their relative importance and variability. This approach may also reveal which organisms and tissues are most susceptible to decay and which are most likely to be fossilised under a given set of conditions. Time scales for fossilisation can be established through laboratory simulations, information that is impossible to glean from fossil material alone (e.g. see **2. 4. 1. 2.** and Martill, 1989 for experimental investigation of the timing of mineralisation of fish from the Cretaceous Santana Formation). Study of modern decayed organisms may also aid the interpretation of problematic fossils, as even the most exceptionally preserved fossils have undergone some degree of degradation (e. g. see Briggs & Kear, 1994b for an elegant taphonomic study of the conodont animal).

Observational and experimental approaches have been applied to archaeological material to some extent but have tended to focus on vertebrate remains, particularly those illuminating hominid activities, e. g. Blumenschine's (1995) study of hammer-stone percussion marks and carnivore tooth marks on long bones in a Plio-Pleistocene bone assemblage. Taphonomic bias has a potentially profound effect on the data used by environmental archaeologists, who deal primarily with plant and arthropod remains, but despite this, there have been virtually no experimental studies investigating the preservation of archaeological biological materials. In the early 1960s, experimental earthworks were established on a chalkland (Overton Down, Wiltshire) and on a gravel heath (Wareham, Dorset) site to explore the longterm weathering and denudation of ditches and banks over time (Ashbee & Jewell, 1998; Lawson *et al.*, 2000). Some biological remains (principally bones, wood and spores) were

among the objects buried in the earthworks, and the movement and condition of these have been monitored at each sampling date (the next excavation of the earthworks will take place in 2024, after 64 years of burial).

Kenward (1976) adopted an actualistic approach to "normalising" archaeological insect assemblages. He investigated the taxonomic composition of modern insect death assemblages in roof gullies and gutters and in bird droppings, in order to establish the background "rain" of insects which needs to be subtracted from any sub-fossil assemblage to give a realistic impression of the local faunal composition. However, differential decay of different species and tissues must also be considered if reliable palaeoenvironmental reconstructions are to be achieved.

CHAPTER 2. FOSSILISATION IN ANCIENT CESS PITS: A STUDY OF BIOLOGICAL REMAINS AND SEDIMENTS FROM DEPOSITS IN AND AROUND YORK

2. 1. Introduction

Ancient cess pits are a valuable source of biological remains dating mainly from the Medieval period to the present day. Their dual function as repositories for organic refuse and latrines has led to the accumulation of seeds, arthropod cuticles, wood and bone fragments which are not often preserved elsewhere. These fossils are extremely important to environmental archaeologists as they reveal information about diet and sanitation and, by implication, agricultural practice, trade, social status and the general health of ancient peoples. In addition, the fossils studied by environmental archaeologists reveal the early effects of diagenetic processes in terrestrial environments, representing a taphonomic stage intermediate between initial decay and diagenetic alteration. The aim of this study was to elucidate the taphonomic processes and conditions associated with the preservation of fossil assemblages in cess pits. Fossils from the three major preservational categories: (1) biomineralised (bones), (2) authigenically mineralised and (3) non-mineralised organically preserved remains (propagules and arthropods), were analysed from a number of ancient cess pits, using a variety of techniques to establish the quality of structural preservation and the associated mineral precipitation and changes in chemical composition. Characteristics of the cess pit sediments were also considered.

2. 2. Materials and methods

2. 2. 1. Introduction

The material analysed in this study comprised sediment samples and fossils, obtained from ancient cess pits during excavations carried out by the Environmental Archaeology Unit (E. A. U.) in York during 1998-1999. Soil samples taken during archaeological excavations are described briefly on-site by the excavators, and these descriptions enabled any samples that obviously contained mineralised faecal concretions to be set aside for analysis in Bristol. The rationale for employing this selection criterion was that these samples would presumably have an increased probability of yielding mineralised as well as non-mineralised remains on sieving, allowing study of a range of preservational styles.

Five sediment samples were obtained, four of which had been recovered from cess pits at St. Saviourgate, a street in York, and a further one from a cess pit at Jack Taylor Lane in Beverley, a village in east Yorkshire. The sediments dated from the 4th to the 16th Century (Table 2. 1.). Throughout this chapter, the site/context/sample numbers for each sample studied are abbreviated to just the sample numbers (i. e. 11, 64, 17, 105 and 15). The biological remains analysed, and the analytical techniques applied to them are summarised in Table 2. 2.

In addition to the fossils recovered from these recently excavated cess pits, mineralised "stable manure" from an archaeological deposit at the 22 Piccadilly (ABC Cinema site), York that had been in storage for twelve years was analysed, along with fossil seeds from a tenth Century cess pit at Coppergate in York, which was excavated some twenty years ago. It was hoped that study of the "ABC Cinema" stable manure would reveal any differences between mineralisation in buried organic deposits such as cess pits, and deposits comprising organic build-ups on stable floors or other

level surfaces. Crab apple seeds from Coppergate were selected for analysis because they display an intriguing combination of a mineralised embryo and an organically preserved seed coat, and were unique within their deposit in showing any mineralisation at all. In addition, blackberry

Table 2. 1. The ages of the cess pit and "stable manure" samples studied

Site	Site/context/sample code	Age
Coppergate, York	76-81.7/18529/1019	10th Century
Jack Taylor Lane, Beverley	BJT98/213/11	13th-14th Century
St. Saviourgate, York	95.434/3105/105	4th Century
St. Saviourgate, York	95.434/2037/64	12th-13th Century
St. Saviourgate, York	95.434/1064/17	16th Century
St. Saviourgate, York	95.434/1059/15	16th Century
22 Piccadilly, York	87.21/2082/71	14th-15th Century

endocarps from the same sample, which were entirely organically preserved, were studied to assess the general level of organic preservation in the cess pit.

Modern reference specimens were also analysed to aid interpretation of the fossil material. To allow comparison of bone preservation in the cess pits with better drained archaeological sediments, human bones from a contemporaneous graveyard at Barton-on-Humber were analysed along with the cess pit material.

2. 2. 2. Sites and fossils studied

2. 2. 2. 1. The Coppergate excavation

Extensive archaeological excavations carried out at 16-22 Coppergate in York between 1976 and 1981 revealed deposits ranging from Roman (late 1st to late 4th Century or later) to late medieval in age. The bulk of the sediments uncovered ranged from mid-9th to mid-11th Century in age, marking the Viking occupation of York (Hall, 1984).

Site:	Taxon/structure:	Py-GC/MS	SEM	EDX	ICP-MS/AES	XRD	Quantified proteins	Quantified sugars	TOC, H & N
Coppergate	Crab apple/pips	5	10	2	6	NA	NA	NA	4
Modern ref.	Crab apple/pips	5	5	NA	6	NA	NA	NA	5
Coppergate	Blackberry/endocarp	6	NA	NA	NA	NA	NA	NA	6
Modern ref.	Blackberry/endocarp	6	NA	NA	NA	NA	NA	NA	6
St. Saviourgate	Corncockle/seed coats	30 (3)	20 (3)	NA	NA	NA	30 (3)	30 (3)	NA
Jack Taylor Lane, Beverley	Corncockle/seed coats	10	8	NA	NA	NA	10	10	NA
Modern ref.	Corncockle/seed coats	8	6	NA	NA	NA	10	10	NA
St. Saviourgate	Beetles/elytra	2	NA	NA	NA	NA	NA	NA	NA
Jack Taylor Lane, Beverley	Beetles/elytra	1	NA	NA	NA	NA	NA	NA	NA
Modern ref.	Beetle/elytra	1	NA	NA	NA	NA	NA	NA	NA
St. Saviourgate	Diptera/puparia	2	NA	NA	NA	NA	NA	NA	NA
Modern ref.	Diptera/puparia	2	NA	NA	NA	NA	NA	NA	NA
St. Saviourgate	Centipede/tergites	NA	1	NA	NA	NA	NA	NA	NA
St. Saviourgate	Woodlice/tergites	NA	6 (2)	NA	NA	NA	NA	NA	NA
St. Saviourgate	Earthworms/min.	NA	6 (2)	3 (2)	NA	NA	NA	NA	NA
Modern ref.	Earthworms	NA	1	NA	NA	NA	NA	NA	NA
St. Saviourgate	Maggots/min.	NA	6 (2)	3 (2)	NA	NA	NA	NA	NA
Modern ref.	Bluebottle maggots	NA	6	NA	NA	NA	NA	NA	NA
Modern ref.	Manduca/cuticle	7	7	NA	NA	NA	NA	NA	NA
St. Saviourgate	Min. faecal concretion	NA	NA	2	4	NA	NA	NA	NA
Beverley	Min. faecal concretion	NA	NA	1	1	NA			
St. Saviourgate	Fish/mammal bones	NA	NA	NA	NA	9(5)	NA	NA	NA
Beverley	Fish/mammal bones	NA	NA	NA	NA	2	NA	NA	NA
Barton-on-Humber	Human bones	NA	NA	NA	NA	39	NA	NA	NA

Table 2. 2. Summary of the biological remains analysed from archaeological sites (York and Barton-on-Humber) and as modern reference specimens, and the analytical techniques applied to them. Figures in columns indicate the number of specimens subjected to each analytical procedure (figures in brackets indicate the number of different archaeological samples from which specimens were derived).
Abbreviations: NA = not applicable (analytical procedure not applied to these specimens).
Modern ref. = modern reference specimens. Min. = mineralised. Py-GC/MS = flash pyrolysis-gas chromatography/mass spectrometry. SEM = scanning electron microscopy. EDX = energy dispersive x-ray analysis. ICP-MS/AES = Inductively-coupled plasma-mass spectrometry/atomic emission spectroscopy. TOC, H & N = total organic carbon, hydrogen and nitrogen.

Numerous biological remains were obtained from the excavation as a whole, but these were particularly abundant in the large number of cess pits uncovered. Mineral replaced remains were recovered only from cess pits and comprised oat (*Avena* sp.) grains, field bean (*Vicia faba*) cotyledons and testa fragments, sloe or plum (*Prunus* sp.) stones, and crab apple (*Malus sylvestris*) pips. The context studied (18529) was recovered from a cess pit (18490) dating from Period 4B (930-935 to c. 975 AD). This context was selected because it contained both mineral replaced and organic fossils, providing an opportunity to study contrasting modes of preservation, in some cases within the same specimen. Period 4B is characterised by a series of post and wattle structures erected along the Coppergate street frontage, demarcating four tenements (designated A, B, C and D) with their gable ends facing what is thought to have been the first street there. Pit 18490 was situated in the back yard of Tenement A, and was approximately 1.5 m in diameter and 1.75 m deep, with wattle lining the upper part. A typical cess pit infill was recovered from a bulk-sieved sample (1019) from Context 18529, a dark olive-grey structured peat immediately overlying the basal layer (18538) of the pit.

The bulk of the context consisted of faecal material which yielded a large assemblage of plant taxa. Most abundant were sloe and plum stones (*Prunus spinosa* , *P. domestica*), and wheat or rye (*Triticum/Secale*) bran, but several other taxa were relatively common: *Rubus fruticosus* (blackberry), *Crataegus monogyna* (hawthorn), *Malus sylvestris* (crab apple) pips and the mosses *Neckera complanata* and *Isothecium myurum*. Most of the plants present were edible species, although weeds, woodland and hedgerow plants were also recorded. Predictably, faecal concretions were fairly common, comprising mineralised lumps which sometimes yielded small numbers of parasitic worm ova

(*Trichuris* and *Ascaris*). Traces of feathers and wool fragments were also recorded, as well as possible examples of charred bread, daub, and dog coprolite, indicating that the pitfill included waste from the surrounding yard and from the tenement floor.

2. 2. 2. 2. Coppergate fossil material studied

Taphonomic analysis of the Coppergate plant assemblage focused on the crab apple pips, which provided the opportunity for study of organic (seed coats) and mineralised (embryo) preservation in the same material. Blackberry seeds (endocarps) were also analysed to provide an independent assessment of the organic preservation of the assemblage.

2. 2. 2. 3. The excavations at St. Saviourgate and 22 Piccadilly ("ABC Cinema"), York and Jack Taylor Lane, Beverley

The other York samples investigated were uncovered during standard archaeological assessments of sites prior to their re-development, so that only a general overview of the sites' archaeology could be obtained with the allocated time and resources.

In 1997, an archaeological survey was carried out at St. Saviourgate in York by MAP Archaeological Consultancy Ltd., comprising excavation of three trenches which revealed deposits ranging in age from Late Roman (?4th Century) to modern (Carrott *et al.*, 1998a). The deposits uncovered comprise mainly pit fills (from both cess pits and refuse pits) and dumps, which generally yielded sediments rich in well-preserved organic remains. Preservation was mainly as "waterlogged" remains, although localised mineralisation was found in some of the cess pits.

Excavations were carried out in 1987 at 22 Piccadilly in York (ABC Cinema site) by the York Archaeological Trust (Carrott *et al.*, 1995). Excavation of four trenches revealed deposits ranging from Roman to

medieval in date. The vast majority of the deposits uncovered at this river-side site comprised dumps or build-ups, some identified as natural sediment deposited by flooding, and others as anthropogenic, comprising the deliberately deposited remains of a variety of human activities (stable manure, butchery waste, food waste, waste from textile dyeing). The sample studied here (from Context 2082) comprised "compressed herbaceous detritus", interpreted as stable manure, and was recovered from Period 6 (dated to the 14th-15th Century). Mineralisation of this sample is thought to have occurred post-excavation, during storage of the sediment, and a possible explanation for this is discussed in **2. 4. 1. 3.**

The Humber Archaeology Partnership carried out archaeological excavations at Jack Taylor Lane in Beverley, Yorkshire during 1998 (Carrott *et al.*, 1998b). The six excavation trenches revealed deposits ranging in date from Medieval to post-Medieval. The deposits uncovered on this water-side site comprise a fen peat, various pit fills and build-ups of waste from human activities (including textile and leather working, wool cleaning and flax retting) that were dumped into a body of water. The sample studied here (11) was recovered from a 12th/13th Century cess pit context (213). This context was interpreted as "almost pure faecal material" and displayed localised mineralisation of faecal concretions.

2. 2. 2. 4. Fossils studied from St. Saviourgate and Beverley

The relative abundances of the fossils recovered (by the author and at a later date by the E. A. U.) from sieving the sediment samples recovered from recent cess pit excavations are listed in Appendix 1. Seeds of a varying mix of taxa were recovered from all of the contexts. Fragments of the virtually ubiquitous, distinct black seed coats of *Agrostemma githago* (corncockle) were collected in significant numbers from all but the oldest of the cess pit samples (Sample 105; dated to the 4th Century A.D.) which

totally lacks them. Beetle elytra were recovered by the author in various numbers from three of the samples (11, 15 and 17), dipteran pupal cases from two (15 and 17), and mineralised invertebrates (woodlice, dipteran pupae, earthworms and a centipede) were recovered from the two 16th Century A. D. samples (15 and 17). Later processing of sample 105 by the E. A. U. yielded small numbers of beetle elytra and fly puparia. Fish and mammal bones and bone fragments were present in various quantities in all of the samples.

The "ABC Cinema" stable manure contained various stems and straws, and a fragment of one of these was analysed along with the fossils from the other sites.

2. 2. 2. 5. The excavation of St. Peter's Churchyard, Barton-on-Humber

The Church of St. Peter in Barton-upon-Humber, North Lincolnshire, is renowned as one of the best examples of an Anglo-Saxon church in England, although much of the original tenth Century building was remodelled during the subsequent Medieval period (Bryant, 1994). Extensive excavations of both the interior of the church and part of its surrounding graveyard were carried out from 1978 until 1985, revealing the largest assemblage of skeletons unearthed in an English parish churchyard (Atkins *et al.*, 1997). The skeletal remains represent a continuous period of burials from the 10th to the 19th Century, and total almost 3000 articulated skeletons, in addition to substantial amounts of isolated bones. Five burial phases were recognised at St. Peter's: A, C10th-C11th; B, C12th-C13th; C, C14th-C15th; D, C16th-C17th; and E, C18th-C19th. A major palaeopathological study of the skeletal material, led by Dr Juliet Rogers of the Rheumatology Unit, University of Bristol, has been in progress for several years. The study has investigated the demography of the Barton-on-Humber population, as well as various

aspects of their health (including pituitary tumours, osteoarthritis, osteoporosis, child growth rate, fractures and diet) through the different phases of the deposit.

2. 2. 2. 6. The bones studied from St. Peter's Church, Barton-on-Humber

The bone samples analysed comprised fragments of human ribs recovered from graves at St. Peter's Church, Barton-on-Humber. This site was selected because a large number of samples were available from different, well constrained time periods and, although the human skeletons were deposited in well-drained soil, a mixture of coffined and non-coffined burials created two distinct hydrological regimes for comparison with the cess pits, which are likely to have been waterlogged for much of the time.

Twenty-two of the samples studied date from the first burial phase at St. Peter's (A: 10th-11th Century) and seventeen from the fifth (E: 18th-19th Century). Skeletons from these two phases were selected for analysis to investigate the impact of length of period of burial on bone preservation. Twenty-seven of the samples were obtained from skeletons which were buried in coffins and twelve from non-coffined skeletons. The distribution of coffined and non-coffined samples by age is given in the table (2. 2.) below.

Table 2. 3. Numbers of Barton-on-Humber bones analysed from each age and burial type category.

Date	Number of coffined samples	Number of non-coffined samples
10th-11th Century	14	8
18th-19th Century	13	4

2. 2. 3. Sediment processing

2. 2. 3. 1. Recovery of biological specimens

Sub-samples (approximately 2 kg) of cess pit sediments selected for analysis from recent E. A. U. excavations were processed in the Department of Earth Sciences, University of Bristol, in addition to their standard environmental analysis and description by the Environmental Archaeology Unit, York. Approximately 1kg of each sediment sub-sample was sieved (by washing through 500 µm and 250 µm aperture sieves) and the residue examined under a binocular light microscope to detect the biological remains present. In addition, small volumes of the residue from the 250 µm sieve were suspended in water in a petri dish to allow the recovery of additional seed coats and beetle elytra by flotation. Plant remains selected for taphonomic analysis were identified by Vanessa Straker, Department of Geography, University of Bristol. The unsieved portions of the sediment samples were kept refrigerated in sealed plastic bags for analysis at a later date.

2. 2. 3. 2. Grain size distribution

To obtain a grain size distribution for the raw sediment samples, approximately 150 g of each sediment sample was placed in a foil container and dried overnight in an oven at 103°C. After cooling in a desiccator, 100 g dry weight of each sample was ground lightly with a mortar and pestle to disaggregate lumps without breaking up individual particles. Each ground sample was then placed on a stack of sieves (with 2 mm, 1 mm, 500 µm and 212 µm apertures) and shaken for 15 min. to separate coarse and fine sand fractions. The sample from each sieve was collected and weighed to obtain the percentage mass in each particle size bracket. The sediment portion recovered from the collecting tray (with a grain size < 212 µm) was later analysed in the Department of Geography,

University of Bristol, using a Malvern Instruments MASTERSIZER, which produces a grain-size distribution for fine sand, clay and silt-sized particles.

2. 2. 3. 3. Soil solution extraction and analysis

As a proxy for the original pore waters in the cess pits, soil solutions were extracted from the sediment samples using centrifugal filtration (after Adams *et al.*, 1980). To ensure sufficient solution yield, the sediments were re-hydrated to field capacity before extraction. The samples were air dried for four days, then 10 g of each uncompacted dry sediment was sprinkled on top of 2 ml of water in a glass graduated cylinder. The tops of the cylinders were sealed to prevent evaporation and left at room temperature for 48 hours. The field capacity of each sediment was then calculated by measuring the movement of the wet front up the sediment column and calculating the volume of water required to re-hydrate all of the sediment in the cylinder. Using the calculated field capacities, 25 g of each air-dried sample was re-hydrated using Milli-Q Water, covered and left to re-hydrate for seven days. The re-hydrated samples were then air-dried again, re-hydrated and left for a further seven days before extraction. The solutions were extracted using Whatman VectaSpin 20 Centrifuge Tube Filters with Anopore Plus (0.2 μm pore size) membranes and pre-filters. Either 20 or 25 g of sediment was used to fill the sample compartment, depending on sample density, and the tubes were then centrifuged for 30 min. at 3000 rpm (equivalent to a force of 1500 g at the base of the soil column). The solution yield ranged from 1.5 ml to 4 ml. The pH of each solution was measured immediately after extraction using a glass electrode, and ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy) was carried

out on the solutions within twenty-four hours of extraction to determine their elemental composition.

2. 2. 3. 4. Total organic carbon, hydrogen and nitrogen analysis

A small volume of each raw sediment sample was ground using a pestle and mortar, and submitted to the Microanalytical Laboratory, School of Chemistry, University of Bristol, for total organic carbon, hydrogen and nitrogen analysis by conventional techniques (using a Perkin Elmer 240C elemental analyser).

2. 2. 4. Assessment of structural preservation of the fossils (using SEM)

Structural preservation of the plant and arthropod fossils was investigated using Scanning Electron Microscopy (SEM), and compared with their living equivalents to aid interpretation. All specimens were examined using a Cambridge Instruments Stereoscan 250 MK III SEM. The mineralised fossils, comprising mainly seeds/grains and fly pupae/earthworms, were mounted entire and/or fragmented onto aluminium stubs and sputter-coated with gold. Entire and sectioned, freeze-dried modern earthworms, bluebottle (*Calliphora*) puparia and larvae were examined under SEM to aid interpretation of the mineralised invertebrates. *Calliphora* larvae which had been decayed in the laboratory for two weeks and then freeze-dried were also examined to aid interpretation of fossil textures thought to have developed during decay (see **2. 2. 8. 2.**).

The non-mineralised fossils (seed coats and beetle elytra) were freeze-dried before examining under SEM. Attempts to section freeze-dried fossil Corncockle seed coat fragments for SEM proved futile because of their brittle nature. Instead, the modern and fossil seed coat fragments were mounted flat on aluminium stubs using silver dag adhesive, so that

only the outer surface of the testa was visible. The beetle elytra were mounted in the same way. A non-mineralised centipede fragment within a mineralised faecal concretion was mounted entire onto an aluminium stub without freeze-drying.

Coppergate crab apple pips were prepared for SEM by fragmenting them onto adhesive carbon discs on aluminium stubs and sputter-coating with gold. Critical point dried and freeze dried modern pips were fragmented in the same way or sectioned to aid interpretation of the fossil tissues.

2. 2. 5. Mineralogical and elemental analysis of the mineralised fossils

The mineralogy of the mineralised fossils was established using EDX (Energy Dispersive X-ray) analysis, and the elemental composition of mineralised concretions from each sediment sample and the "ABC Cinema" mineralised stable manure was established using ICP-AES (Inductively Coupled Plasma - Atomic Emission Spectroscopy) and ICP-MS (Inductively Couple Plasma - Mass Spectrometry). In preparation for ICP-AES, a mineralised faecal concretion from each of the four freshly excavated York cess pits, in addition to mineralised faecal material and a mineralised straw recovered from the floor of the "ABC Cinema" stable, and a number of Coppergate mineralised crab apple seed embryos were ground up and digested using 1% (v/v) nitric acid. The major elements (P, Ca, Na, Mn, Mg, Fe and K) were then measured quantitatively using ICP-AES (inductively coupled plasma-atomic emission spectroscopy). A preliminary, semi-quantitative ICP-MS analysis of all minor elements in the embryos revealed those showing significant variation from modern embryos, and these were then measured quantitatively (ICP-MS).

2. 2. 6. Chemical analysis of the organic fossils

The chemical compositions of the non-mineralised remains (seed coats, beetle elytra and fly puparia) were compared with those of their modern equivalents using Py-GC/MS (flash pyrolysis-gas chromatography/mass spectrometry). This technique was selected because it is non-specific, revealing a range of biomacromolecules rather than targeting specific ones. Hence, it does not require any foreknowledge of composition, which can vary significantly, particularly between the coats of different seed species. In addition, only a small sample size is required (μg quantities), making this an ideal technique for use with relatively scarce fossil material. Corncockle (*Agrostemma githago*) seed coats were selected as an indicator of organic plant preservation in the recently excavated cess pits, as they are virtually ubiquitous in ancient cess pits and were absent only from the 4th Century St. Saviourgate pit sample (105) in this study. Crab apple (*Malus sylvestris*) seed coats and blackberry (*Rubus fruticosus*) endocarps were analysed from the Coppergate sample. Beetle elytra from the 13th/14th Century Beverley pit (11) and the two 16th Century St. Saviourgate pits (15 & 17) were also studied, in addition to dipteran puparia from samples 15 and 17. A quantitative measurement of the proteins present in the corncockle seed coats was achieved using acid hydrolysis and derivatisation of amino acids, which were then separated and identified using GC-MS. A similar technique was used to quantify the carbohydrates in the corncockle seed coats, which were separated and identified using GC.

2. 2. 6. 1. Flash pyrolysis-gas chromatography/mass spectrometry (py-GC/MS)

In preparation for py-GC/MS, modern corncockle, crab apple and blackberry seeds, and modern and fossil beetle elytra were freeze-dried. The seed coats were mechanically removed from fossil and modern seeds and all samples were solvent extracted using CH_3OH and CH_2Cl_2 (1: 1, 1: 2 and 0: 2 v/v).

Py-GC/MS was carried out using a CDS (Chemical Data System) 1000 pyroprobe, connected to a Carlo Erba 4130 GC coupled to a Finnigan 4500 MS. Compounds were separated using a 50 m CP Sil-5 CB column (0.32 mm i.d., film thickness 0.4 μm). Each sample was loaded into a quartz tube and pyrolysed in a flow of helium for 10 s at 610°C. The pyrolysis interface was held at 250°C and the GC injector maintained at 250°C. The temperature of the GC/MS transfer line was set at 310°C. The GC oven was operated under the following program: isothermal for 5 min at 35°C; temperature programmed at $5°C min^{-1}$ to 310°C; and then isothermal for 10 min. The MS was operated in full scan mode (40-650 Da, 1 scan s^{-1}, 70 eV electron energy, 300 mA emission current, and ionisation source temperature of 170 °C).

2. 2. 6. 2. Quantitative measurement of proteins in the seed coats

A quantitative measure of the degradation of proteins in the corncockle seed coats was achieved using acid hydrolysis and derivatisation of amino acids, which were then separated using GC/MS.

Acid hydrolysis of proteins (after Hunt, 1985)

Approximately 1 mg of each specimen was weighed and placed in a reaction tube (1 ml). To hydrolyse the peptide bonds linking the amino acids, 6M HCl was added to the sample in a 1:500 w/v (i. e. approximately

0. 5 ml). The tube was then evacuated by connection to the house vacuum and sealed with a Teflon-lined cap to exclude the majority of dissolved oxygen, which can cause loss of products through oxidation, and left at 100°C for 24 h. The excess acid was evaporated off (at 40°C) using a stream of N_2 and the hydrolysate was then transferred to a Pyrex tube (13 mm x 100 mm) with a Teflon-lined cap (3 x 0.5 ml H_2O and 3 x 0.5 ml MeOH). -amino-n-butyric acid (internal standard; 10 µl of concentration 0.61µg µl $^{-1}$) was added to each tube and rinsed down 3 times using dd H_2O. The tubes were then centrifuged at 1000 rpm for 15 min., and the supernatant removed to new tubes. The solvents were then removed by evaporation (40°C under a stream of N_2).

Isopropyl-esterification of amino acids and protein hydrolysates using 4M isopropanoic HCl (after Islam & Darbre, 1972; Darbre & Blau, 1965).

Isopropanoic HCl solution (2 ml, 4M) was added to the hydrolysate (mg quantity) and heated to 70°C for 60 min. in a Pyrex tube with a Teflon-lined cap. After cooling, excess reagents were removed by evaporation (40°C under a stream of N_2). Aliquots of dichloromethane (3 x 0. 5 ml) were added and evaporated to remove excess methanol and water.

Trifluoroacetylation of amino acids and protein hydrolysates using trifluoroacetic anhydride (TFAA) (after Darbre & Blau, 1965; Darbre & Islam, 1968; Blau & Darbre, 1993).

TFAA (*ca* 0.2 ml) was added to the amino methyl-esters in a Pyrex tube (13 mm x 100 mm) sealed with a Teflon-lined cap and left at room temperature for 30 min. The excess reagents were then removed by evaporation (-20°C under a stream of N_2). The products were then dissolved in an appropriate volume of DCM (usually 1 ml for large samples or standards, otherwise 100 µl) for separation using GC-MS.

The GC oven was initially held at 35°C for 4 minutes before increasing the temperature to 200°C at a rate of 5°C min^{-1}. The temperature was held at 200°C for 10 min. The amino acids were identified based on their mass spectra and retention times with reference to standards.

Quantities of amino acids detected in the samples were corrected for loss during hydrolysis using correction factors from Darragh *et al.*, (1996) (Table 2. 4.).

Table 2. 4. Corrections in amino acid quantities for inherent loss during hydrolysis (after Darragh *et al.*, 1996). N/A indicates that no value is available.

Amino acid	Actual value	Value apparent after hydrolysis	Correction multiple
Alanine	12	11.3	1.06
Glycine	12	10.4	1.15
Threonine	7	6.3	1.11
Serine	10	8.4	1.19
Valine	6	5.8	1.03
Leucine	8	7.5	1.07
Isoleucine	6	5.4	1.11
Proline	N/A	N/A	N/A
Hydroxyproline	N/A	N/A	N/A
Aspartic acid	21	20.5	1.02
Glutamic acid	5	5.3	1.02
Phenylalanine	3	3.2	0.94
Tyrosine	3	2.8	1.07

2. 2. 6. 3. Quantitative measurement of the carbohydrates in the seed coats (after Blakeney *et al.*, 1983).

The carbohydrates in the corncockle seed coats were quantified using acid hydrolysis and derivatisation of the monosaccharides, which were then separated using gas chromatography and identified using their GC retention times. The procedure used was as follows:

Approximately 1mg of each sample was weighed into a Young's Tube, 50 μl of 72% H_2SO_4 was added, and the tubes were vortex mixed and left at room temperature for 1 h, mixing often. Five hundred microlitres of DCM-extracted dd H_2O was then added to each tube and vortex mixed, before leaving for 2 to 3 h in a heated block at 110°C. After cooling, each sample was filtered through a cotton wool plugged pipette. Two microlitres of the internal standard pentaerythritol (20 mgl^{-1}) was added to each sample, followed by 2 ml of a 1: 4 v/v mixture of N-Methyldi-*n*-octylamine and chloroform. The samples were thoroughly vortex mixed, and allowed to settle into two layers.

The top layer was removed and passed through a cotton wool plugged pipette. A small amount of water was added to each original sample tube, vortex mixed and again allowed to settle into two layers. The top layer was once more removed and passed through the cotton wool column. $NaBH_4$ (2 ml) was added to each collected filtered solution and these were then placed in a heated block (40°C) for 90 min. 300 μl glacial acetic acid was then added to each sample tube, followed by 1ml acetic anhydride and 0.2 ml methyl imidazole. The tubes were thoroughly vortex mixed and allowed to stand for 10 min at room temperature. Each tube was filled with DCM-extracted dd H_2O, ~5 ml of diethyl ether were then added, and they were shaken up manually, leading to separation of two layers. The top layer was removed to a small vial and this process (adding diethyl ether, shaking and removing top layer) was repeated three times. The samples were then blown down under nitrogen, before being re-dissolved in approximately one third of a vial of water (DCM-extracted dd). Diethyl ether was added and the top layer removed three more times, with the top layer passed through an $MgSO_4$ column each time. The samples were blown down under N_2 once more and were then dissolved in 200 μl DCM in preparation for GC analysis. The samples were run on an SGE BPX-70

column (25m x 0.32mm x 0.25μm) and the GC oven was operated using the following temperature programme: 50°C for 1 minute, then to 150°C at 20°C /min, followed by 180°C at 4°C/min, and finally to 215°C at 3°C/min.

2. 2. 7. Analysis of bone crystallinity

Bones (fish and mammal) from each of the sieved sediment samples were analysed using XRD (X-ray diffraction) analysis to establish the extent of hydroxyapatite alteration. XRD analysis is the tool most commonly used to study the diagenetic alteration of hydroxyapatite, which in fossil bone appears as three diffuse maxima or peaks located between 30° and 35° 2θ on the X-ray diffractogram. A very diffuse diffractogram is obtained for fresh bone, in which it is very difficult to distinguish the individual maxima (Figure 2. 1). It is well documented that bone diagenesis is marked by a progressive increase in the sharpness of the apatite peaks, which has been variously attributed to an increase in the size and perfection of the apatite crystallites (Bartsiokas & Middleton, 1992), their dissolution and recrystallisation (Hassan *et al.*, 1977; Kyle, 1986; Schoeninger *et al.*, 1989), precipitation of geological apatite on and within the bone tissue (Schoeninger, 1982), or to ionic exchange with fluorine (Perinet *et al.*, 1975). The crystallinity of bone can be quantified by calculating a Crystallinity Index (C. I.). Although the C. I. can be calculated in a number of different ways, the nature of the results obtained in this study necessitated calculation of the crystallinity index by measuring the full width of the main apatite peak at half its maximum height (FWHM; after Hedges *et al.*, 1995).

To gain an insight into how the preservation of cess pit bones compares with that of bones from other types of archaeological deposit,

fragments of human ribs from graves at Barton-on-Humber were also analysed.

Depending on size, the entire bone or a fragment of it was ground using a pestle and mortar to produce a powder which was fine enough to pass through a 63 μm sieve. The powder was suspended in acetone and poured onto an XRD slide to leave a thin film of bone on drying. Small fragments of human ribs from the graveyard at Barton-on-Humber, dating from the 10th-11th and 18th-19th centuries, were prepared and analysed in the same way.

The parameters of the XRD programme used to measure the bone crystallinity are summarised in Table 2. 5.

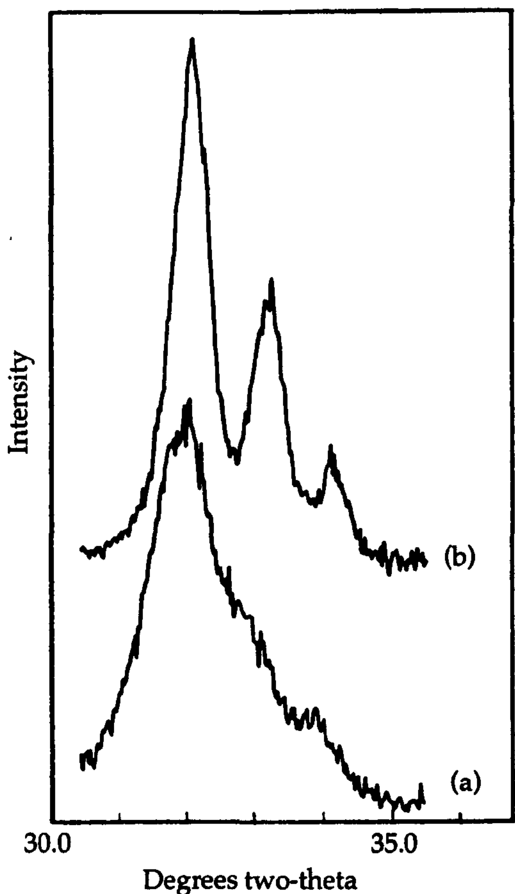


Figure 2. 1. XRD patterns of bones. (a) modern human bone, and (b) *Homo erectus* bone, approximately 1.6 million years old, showing the increased sharpness of the three major hydroxyapatite maxima in fossil bone.

Table 2. 5. Parameters of the XRD programme used to measure the crystallinity of the fossil bones.

Programme	Step size	Start Angle	End Angle	Time per step (s)	Scan speed
crystallinity and carbonate con.	0.005	24.000	36.000	1.000	0.005

2. 2. 8. Laboratory decay of modern arthropods

2. 2. 8. 1. Decay of *Manduca sexta* pupal exuviae cuticle

Laboratory decay of the cuticle of horn worm (*Manduca sexta*) pupal exuviae was carried out under fresh water conditions to provide a standard against which to assess the preservation of arthropod cuticles recovered from the ancient cess pits. Since the cuticles recovered from the ancient cess pits comprise beetle elytra and dipteran pupal cases, it was hoped that analysis of beetle pupal cases would provide an insight into the preservation of both types of cuticle. Fresh water conditions were used because they are likely to be closer in composition to the pore waters of terrestrial cess pits than is sea water. Isolated cuticle was decayed to remove the relatively long period of time during which microbes use up the soft parts of a carcase, hence forcing them to go directly to using the more recalcitrant cuticle as a nutrient source. The decay experiment was set up as follows:

An inoculum was created by culturing and sub-culturing bacteria in Widdels artificial fresh water (without sulphate; see Appendix 2 for composition) with added sediment (from a freshwater moat, as an initial bacteria source), nutrients and ground *Manduca sexta* cuticle. This procedure aimed to build up a population of bacteria capable of breaking down the cuticle, so that they could be used to inoculate the experimental

vessels at the outset, hence reducing the length of time it would take for these bacteria to establish themselves.

The initial sample size of *Manduca* cuticle used was 750 mg. Allowing for a maximum weight loss of 60% through decay, this sample size gives a sufficient cuticle yield (a predicted minimum of 300 mg) for Py-GC/MS and SEM analyses. Each sample was divided up into 3 x 250 mg sub-samples (each equivalent to approximately 4 or 5 pupal exuviae) because the volume of cuticle needed to make up the required sample mass was judged much too great for a single experimental vessel. Eight sets of 750 mg samples were set up, giving a total of 24 experimental vessels.

Each experimental vessel (an ointment jar of 80 mm diameter and 300 ml volume) initially contained:

75 ml Widdels artificial fresh water (without sulphate), including 4 ml inoculum;

3 ml sediment (from the freshwater moat, as above);

~250 mg *Manduca sexta* cuticle (mass of cuticle in each jar was recorded in mg).

The jars were initially incubated at 19°C. The jars were set up on Monday 27th April 1998, and the preliminary sampling dates set as:

11th May 1998 (2 weeks)

25th May 1998 (4 weeks)

22nd June 1998 (8 weeks)

17th August 1998 (16 weeks)

7th December 1998 (32 weeks),

19th July 1999 (64 weeks).

Eight samples were set up so that sampling could be carried out between or beyond these 6 preliminary sampling dates, in the event of decay occurring rapidly or very slowly.

On each of the first three sampling dates, two experimental jars were terminated by filtering the jar contents and retrieving the cuticle. Negligible weight loss by decay was predicted at this stage so that the cuticle yield from two jars was sufficient for analysis. The cuticle fragments were gently rinsed in water to remove any adhering sediment and freeze-dried, in preparation for analysis. Three jars were terminated on subsequent sampling dates to cater for increased degradation of the cuticle.

Pyrolysis-GC/MS analysis of a sample of the cuticle decayed for 16 weeks revealed negligible degradation on the basis of similarity to fresh cuticle SEM micrographs and pyrograms, indicating that the temperature at which the jars were being incubated was too low to produce significant degradation on a reasonable timescale. The temperature was then increased from 19°C to 35°C, in an attempt to accelerate decay rate.

Subsequent sampling and py-GC/MS analysis at 32 weeks revealed little difference from the pyrogram of the 16 weeks decayed cuticle, suggesting that significant degradation had yet to take place. However, changes in the distribution of pyrolysis products relative to the 16 weeks pyrogram were more pronounced than between any two previous samples, suggesting that more dramatic compositional change had taken place, as hoped. Sampling was carried out again at 64 weeks.

2. 2. 8. 2. Decay of *Calliphora* larvae

A surface texture was observed on the mineralised cess pit maggots which is not present on fresh maggots; hence, it was concluded that this texture must represent a diagenetic artefact which arose during decay, and an experiment was set up to attempt to replicate this. *Calliphora* larvae were purchased live from a fishing tackle shop and killed by placing them in a freezer for several hours. Three larvae were placed in each of two

experimental vessels (300 ml volume ointment jars), on top of a 50 mm deep layer of pond sediment (as a bacteria source), with 100 ml of pond water. The lids were closed and the jars were incubated for two weeks at 19°C. After incubation, the larvae were retrieved and freeze-dried for SEM analysis.

2. 3. Results

2. 3. 1. Propagules

2. 3. 1. 1. Macroscopic appearance

Intact corncockle seeds are very rare in the ancient cess pits. The majority of the abundant specimens recovered comprise only seed coat fragments, indicative of accidental milling as a contaminant of flour.

A mineralised indeterminate Poaceae caryopsis (Figure 2. 2. A) and a mineralised *Centaurea* achene, were recovered from mineralised faecal concretions in Sample 64. A mineralised *Triticum* grain (Figure 2. 2. B) was also discovered free-lying in sediment Sample 15. Both of the fossils in the faecal concretions appeared to comprise naked, amber-coloured embryos, with limited, peripheral occurrence of the overlying tissue layers. The *Triticum* grain appeared rather dusty and fragile under the light microscope, with apparently very limited structural preservation.

Superficially, most of the Coppergate seeds appear to be preserved in a pristine condition, although the crab apple seed coats are rough and matt (Figure 2. 2. C), rather than smooth and shiny like their modern counterparts.

Removal of the crab apple seed coat typically reveals a beige to rust coloured mineralised interior, interpreted as the cotyledons of the embryo through comparison with modern pips (Figure 2. 2. D). The hypocotyl and radicle are absent but it is not clear under the light microscope

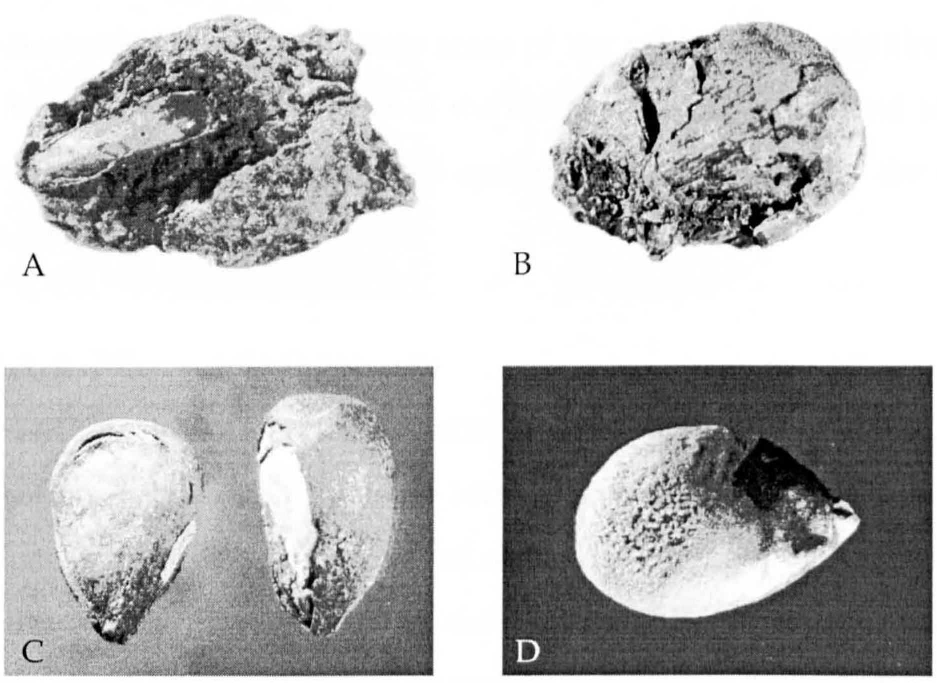


Figure 2.2. Mineralised propagules from archaeological cess pits in York. A. Indeterminate Poaceae grain within faecal concretion from a 16th Century cess pit at St. Saviourgate (x6). B. *Triticum* sp. grain from a 16th Century cess pit at St. Saviourgate (x8). C. Crab apple seeds from a 10th Century cess pit at Coppergate (x6). D. Naked crab apple seed embryo from a 10th Century cess pit at Coppergate (x10).

whether the endosperm, visible as an opaque film covering the embryo in modern seeds, remains. A small proportion of specimens lack a seed coat and comprise just mineralised embryos, whilst in others, mineral replacement extends to include areas of the seed coat, in addition to the embryo. Mineral replacement of the entire seed coat is rare and was only noted in one flattened, wrinkled specimen in which little of the embryo remained.

2. 3. 1. 2. Microscopic appearance

SEM of the mineralised *Triticum* (wheat) grain and *Centaurea* (cornflower/knapweed) achene recovered from the recently excavated sediments reveals a high level of structural preservation, at least on a localised scale. Preservation of the seed coat and pericarp of the wheat grain is patchy and appears to be mainly restricted to replication of the cell walls and mineral infilling of the elongate thickened cells of the inner epidermis (Figure 2. 3. B). In places, apatite spheres with a mean diameter of 10 μm are evident underlying this where the epidermis had broken away. There is some localised occurrence of replicated cell walls of the endosperm tissue (Figure 2. 3. A).

Much of the surface of the *Centaurea* achene is covered by replicated cell walls of the rounded polygonal cells of the endosperm (Figure 2. 3. C). Preservation of overlying tissues is generally restricted to the edges of the achene, where it contacts the surrounding faecal concretion. At the broad end of the achene, three cross-hatched fibrous sclerotic cell layers of the seed coat are preserved, with the longitudinal axes of the cells lying at an angle in adjacent layers (Figure 2. 3. D). Patches of the underlying exotestal palisade layer are visible towards the pointed end of the achene (Figure 2. 3. E & F). This tissue is preserved through replication of the radially elongate cell walls, giving it a fibrous appearance.

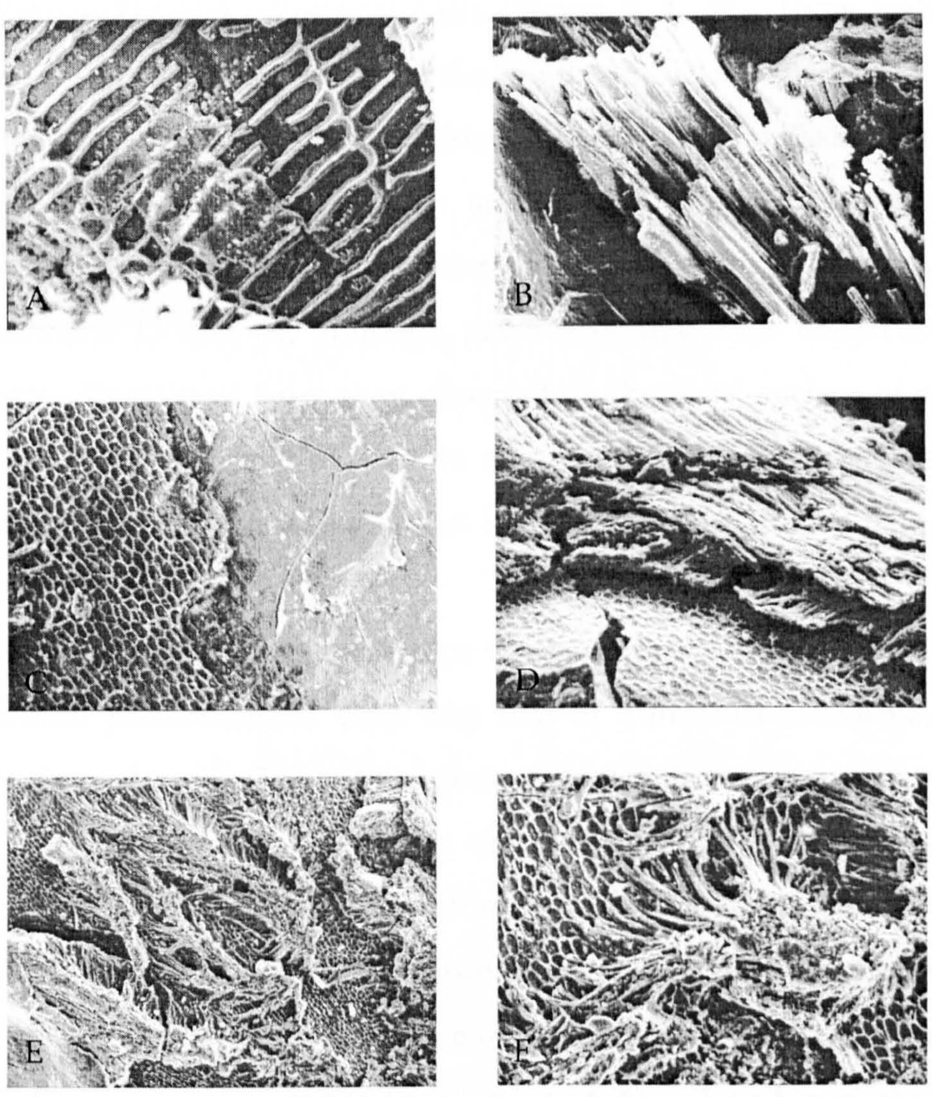
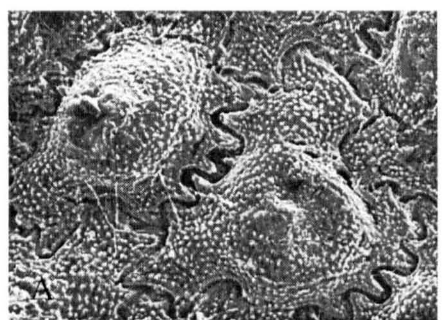


Figure 2. 3. Tissues preserved in mineralised propagules from archaeogical cess pits in York. A. Endosperm cell walls in *Triticum* sp. from 16th Century cess pit at St. Saviourgate (x200). B. Mineralised rods resulting from infilling of sclerotic cell walls in seed coat of *Triticum* sp. grain from 16th Century cess pit at St. Saviourgate (x100). C. Endosperm cell walls in *Centaurea* sp. achene from 16th Century cess pit at St. Saviourgate (x200). D. Endosperm cell walls and overlying cross-hatched structure resulting from replication of cell walls in *Centaurea* sp. achene testa, from a 16th Century cess pit at St. Saviourgate (x200) . E. (x100) and F. (x200) Fibrous structure resulting from replication of radial cell walls in exotestal palisade layer of *Centaurea* sp. achene from a 16th Century cess pit at St. Saviourgate.

In modern corncockle specimens, cell outlines are clearly demarcated by gaps between them on the testa surface, which is covered with micropapillae and occasional hairs (Figure 2. 4. A). These features are preserved to varying extents on the fossil corncockle testae surfaces. The cell outlines in the fossil corncockle seed coats are emphasised by greater gaps between the cells, which are of relatively uniform size in all specimens (Figure 2. 4. B). A micropapillae covering is obvious only in specimens 15 and 64, although patches of this were observed on the others. Occasional hairs were observed on the testal surface of specimen 64 but these were not obvious in any of the other fossils. Overall, the testal surfaces of specimens 11 and 17 appear more degraded than those of specimens 15 and 64.

Ten Coppergate crab apple pips were examined under SEM. The most common preservational state was that of mineralised embryos within organic seed coats. The bulk of these ancient embryos comprises spheres 2 to 20 μm in diameter, commonly clumped and fused to form aggregates and contained within a mineralised membrane with uneven surface relief (Figure 2. 5. A). Comparison with modern pips suggests that this represents the cotyledons of the embryo with their food reserves (Figure 2. 5. B). Evidence for mineral replication of the cell walls was absent in all but one specimen, in which the cellular structure was more or less intact but the nutrient bodies had disappeared. In another specimen, rosettes of mineral needles were observed overlying the spheres in the cotyledon area, and these had isolated spheres on their surface (Figure 2. 5. C).

Overlying the cotyledons is a 100 μm layer of three-dimensional tissue with intact cell walls and spheres (3 to 13 μm in diameter) liberally distributed over the surfaces (Figure 2. 5. D). The fracturing of the tissues observed in this layer is attributed to the preparation technique. In places,



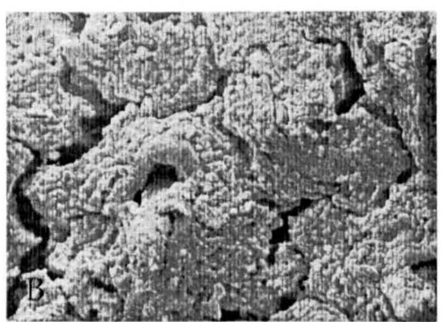


Figure 2. 4. Outer surfaces of corncockle (*Agrostemma githago*) seed coats. A. Modern corncockle seed coat, displaying micropapillae, hairs and gaps between individual cells (x60). B. Fossil corncockle seed coat from a cess pit at St. Saviourgate, York, displaying increased gaps between individual cells, but with micropapillae still obvious (x250).

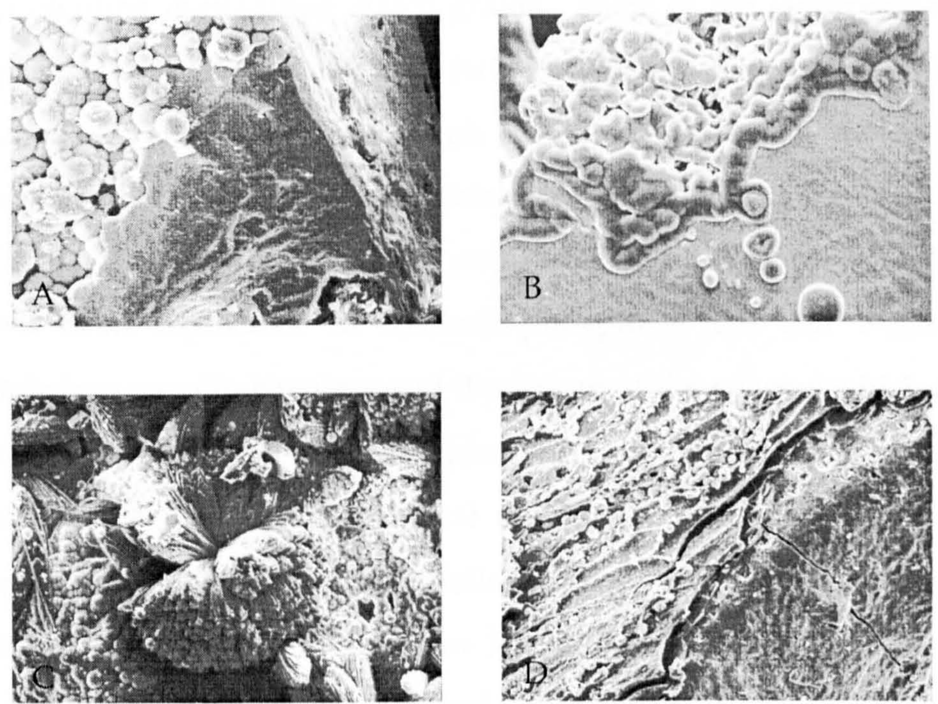


Figure 2. 5. Textures preserved in mineralised crab apple (*Malus sylvestris*) seeds from a 10th Century cess pit at Coppergate, York. A Outer cotyledon membrane containing mineralised nutrient bodies in Coppergate seed (x285). B. Cotyledon membrane and nutrient bodies of modern crab apple seed (x210). C. Rosette of calcium carbonate crystals in Coppergate crab apple seed cotyledon (x150). D. Mineralised endosperm tissue and underlying outer cotyledon membrane in Coppergate crab apple seed (x150).

minute spherules (~2 µm) form a dense covering. This is interpreted as the endosperm tissue of the seed, the 2 µm spherules presumably representing mineralised starch grains. Some of the larger spheres may represent autolithified bacteria (which typically range from 2 to 5 µm; Martill & Wilby, 1993), although the large size range makes it more plausible that these spheres are abiological in origin.

While the endosperm tissue and outer membrane of the cotyledons have been replicated in calcium phosphate, the cell walls of the cotyledons usually have not and the nature of the spheres which typically make up the bulk of the phosphatised cotyledon tissues is equivocal. They may represent the spherical nutrient bodies that fill modern crab apple seed cotyledons and are similar in size (~2-20 mm). The Coppergate spheres have often coalesced to form aggregates, suggesting mineral precipitation beyond the original boundaries of the nutrient bodies. Alternatively, the spheres may have resulted from mineral precipitation at multiple points of origin to infill the void created by decay of the cotyledon tissue. In this case, decay of the nutrient bodies would have promoted mineralisation by creating highly localised concentrations of mineral ions, without dictating the form of the mineral bodies.

In one of the specimens studied, mineral replication of the cotyledon cell walls had taken place, although mineral spheres were absent. Areas of the seed coat were also mineralised, indicating that decay had reached a more advanced stage before phosphatisation was initiated. In specimens with more extensive mineralisation, parallel solid mineralised rods form an outer layer overlying the endosperm (Figure 2. 6. A). These are interpreted as casts of the elongated sclerotic cells that make up the testa (Figure 2. 6. B). The majority of the crab apple seeds retain organic seed coats that are indistinguishable structurally from fresh modern specimens (Figures 2. 6. C & D).

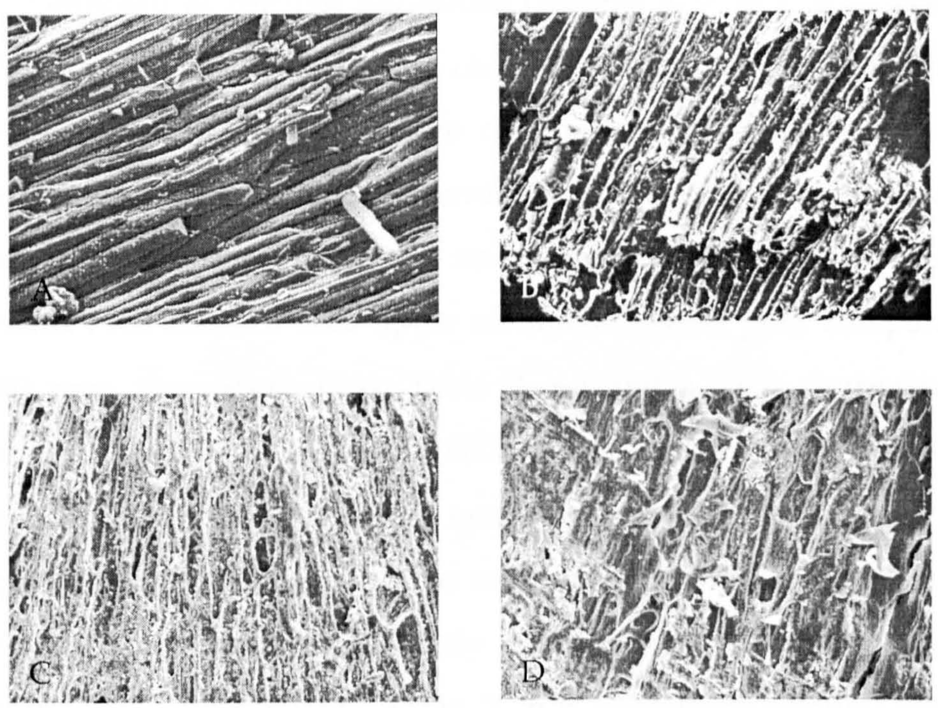


Figure 2. 6. Tissues preserved in fossil crab apple (*Malus sylvestris*) seeds from a 10th Century cess pit at Coppergate, York. A. Mineralised rods created by mineral infilling of sclerotic cells in base of seed coat (x250). B. Fragment of modern crab apple seed coat showing fibrous sclerotic cells (x250). C. Surface view of non-mineralised seed coat of Coppergate crab apple seed (x250). D. Surface view of modern crab apple seed coat (x250).

2. 3. 1. 3. Composition of the mineralised seeds

EDX analysis revealed that the mineralised tissues in the cess pit seeds are composed of calcium phosphate (Figures 2. 7. & 2. 8.). Rosettes of calcium carbonate needles were observed overgrowing the phosphatised tissues in one of the Coppergate crab apple specimens (Figure 2. 5. c). Predictably, ICP-AES analysis revealed that the Coppergate crab apple embryos show a greater than one hundred-fold increase in calcium content over modern crab apple embryos (334000 ppm compared with 2340 ppm in modern pips; Table 2. 6.) and a high concentration of phosphorus was also recorded (156000 ppm, compared with 10500 ppm in modern pips). The difference in the concentration of Ca and P is in approximate agreement with the stoichiometry of apatite. Other major elements are also significantly concentrated in the mineralised Coppergate embryos (see Table 2. 6.): sodium is almost 100x more concentrated than in modern pips, manganese almost 200x and iron almost 250x. Relatively high concentrations of magnesium were also recorded (5700 ppm, compared with 350 ppm in modern pips). Barium and strontium were the only minor elements showing major concentration in the mineralised embryos (see Table 2. 7.).

Table 2. 6. Major elements in modern and Coppergate crab apple seed embryos (ppm = parts per million).

Element	Concentration in modern crab apple seed embryos (ppm)	Concentration in Coppergate crab apple seed embryos (ppm)	Concentration in Coppergate/ concentration in modern
Fe	49	12150	248.0
Mn	29	5500	189.7
Mg	406.5	440	1.1
Ca	2340	334000	142.7
Na	32.5	2965	91.2
P	10500	156000	14.9
K	492.5	473.5	1.0

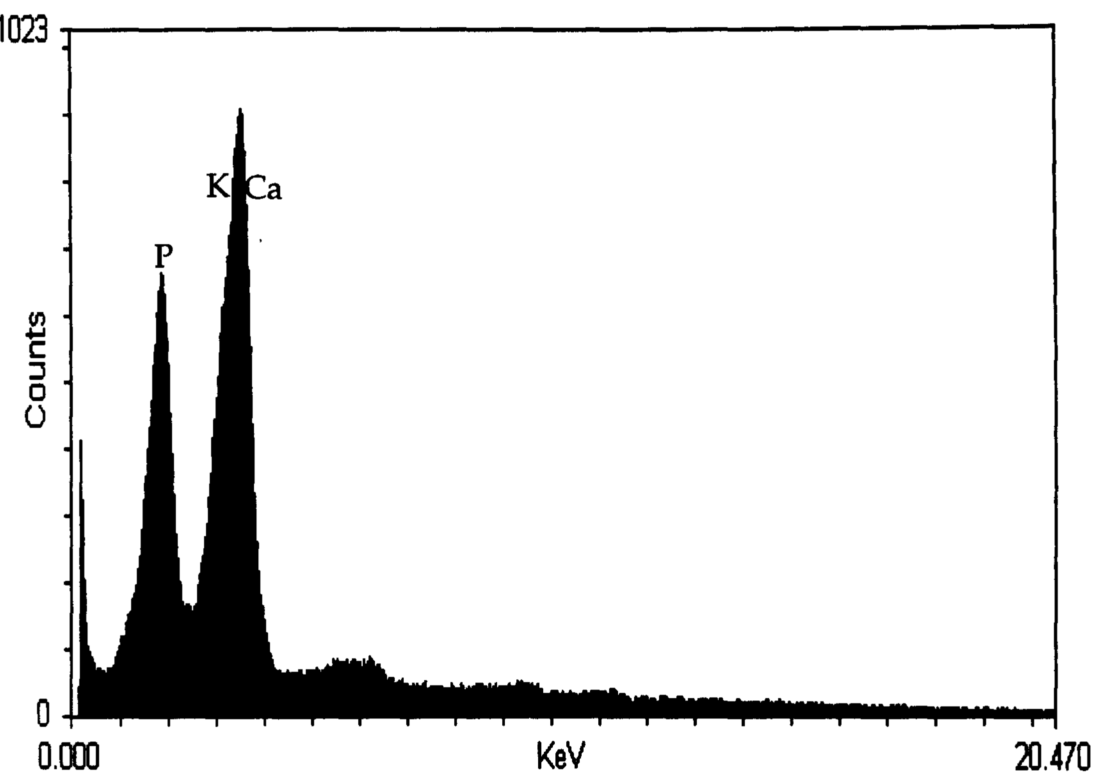


Figure 2. 7. EDX spectrum of a mineralised crab apple seed embryo from a tenth century cess pit at Coppergate, York, showing a calcium phosphate mineralogy.

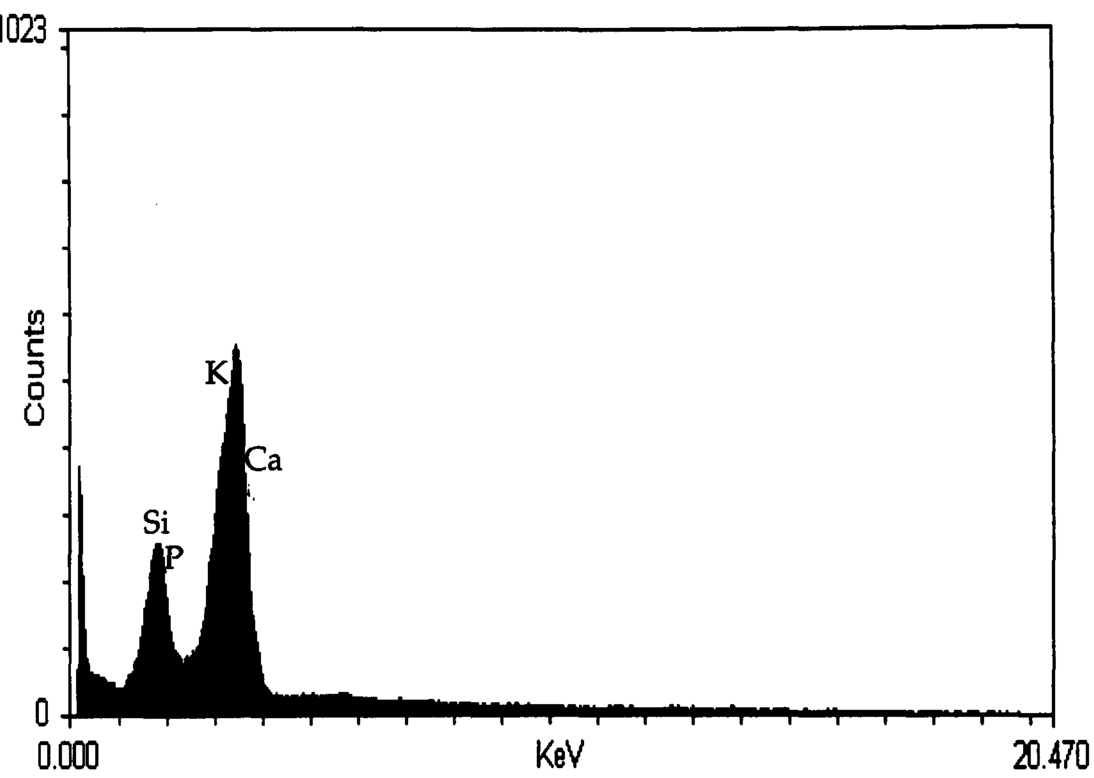


Figure 2. 8. EDX spectrum of a mineralised Centaurea sp. achene from a 16th century cess pit at St. Saviourgate, York, showing a calcium phosphate mineralogy.

Table 2. 7. Minor elements in modern and Coppergate crab apple seed embryos (ppb = parts per billion).

Element	Concentration in modern crab apple seed embryos (ppb)	Concentration in Coppergate crab apple seed embryos (ppb)	Concentration in Coppergate/ concentration in modern
Ge	0.2199	0.7848	3.5694
Sr	2.0733	1152.2474	555.7553
Au	0.6719	3.0072	4.4757
Ba	2.8073	1128.5685	402.0121

2. 3. 1. 4. Composition of the organically preserved propagules

There have been few investigations into the chemical composition of seed coats, despite the fact that these relatively decay-resistant tissues may make a significant contribution to sub-fossil and fossil assemblages. Studies by van Bergen and colleagues (1991, 1994a-c, 1996 and references therein) revealed that in seed coats comprising two distinct layers, the testa (outer seed coat) tends to have a polyphenolic composition, which differs in monocotyledonous and dicotyledonous plants, whilst the tegmen (inner seed coat) is typically highly aliphatic.

2. 3. 1. 4. 1. Pyrolysis-GC/MS results

Figure 2. 9. (a) to (c) shows pyrograms of a modern and two cess pit fossil corncockle seed coats. Figure 2. 10. (a) and (b) show modern and fossil crab apple seed coats, and Figure 2. 11 (a) and (b) modern and fossil blackberry endocarps. The peak numbers on all seed coat pyrograms refer to compounds listed in Table 2. 8. Compounds were identified using GC retention times and published mass spectral data (Galletti & Bocchini, 1995; Ralph & Hatfield, 1991; Stankiewicz *et al.*, 1997b; Boon *et al.*, 1989, van Bergen *et al.*, 1997a).

2. 3. 1. 4. 1. 1. Composition of modern corncockle seed coats

The pyrolysate (Figure 2. 9. (a)) of the modern corncockle (*Agrostemma githago*) seed coat is dominated by the polysaccharide products 3-hydroxy-2-methyl-2-cyclopenten-1-one (**20**), 2-hydroxy-3-methyl-2-cyclopenten-1-one (**22**) and 3-hydroxy-2-methyl-(4H)-pyranone (**30**), in addition to phenol (**19**), 4-methylphenol (**27**) and catechol (**39**). 2-methylphenol (**26**) and the polysaccharide markers 2, 4-pentadienal (**7**), 2-furaldehyde (**8**), 1-acetoxypropan-2-one (**10**), 2, 3-dihydro-5-methyl-furan-2-one (**16**) and 5-methyl-2-furaldehyde (**17**) are also relatively abundant. The typical angiosperm lignin markers guaiacol (**28**), 4-ethylguaiacol (**45**) and 4-vinylguaiacol (**48**) are present in relatively low abundances.

The composition of the modern corncockle seed coat is very different from that of typical dicotyledonous angiosperms, which are dominated by 2-methoxyphenols (guaicyl compounds) and 2, 6-dimethoxyphenols (syringyl compounds). The presence of the characteristic lignin markers guaiacol (**28**), 4-ethylguaiacol (**45**) and 4-vinylguaiacol (**48**) suggests that a ligno-cellulose complex is present in the seed coats. The dominance of compounds which are not exclusive to, and typically do not dominate, lignin pyrolysates suggests that a range of biomacromolecules is present. Indole (**46**) may be derived from the amino acid tryptophan (Tsuge & Matsubara, 1985; Chiavari & Galletti, 1992) and phenol (**19**) and 4-methylphenol (**27**) can be produced by the amino acid tyrosine on pyrolysis (Bracewell & Robertson, 1984; Tsuge & Matsubara, 1985), suggesting a significant proteinaceous component of the seed coats. Catechol (**39**) and 4-methylcatechol (**47**) may be present as minor components of lignin but the dominance of catechol observed in these pyrolysates is not typical of ligno-cellulose tissues (Pouwels *et al.*, 1987; van der Heijden & Boon, 1994). These two compounds are the major products produced by pyrolysis of non-hydrolysable tannin monomers

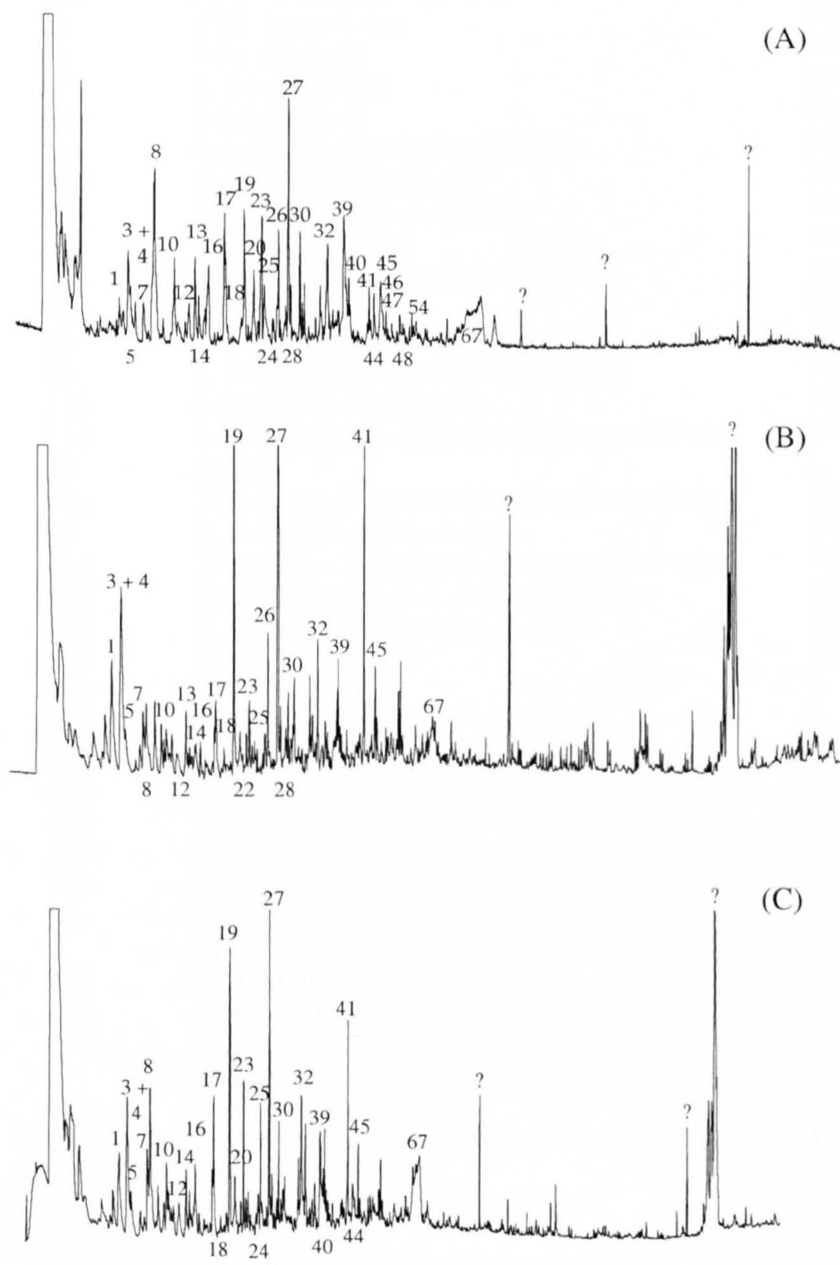


Figure 2. 9. Pyrograms of (A) modern, (B) cess pit fossil (Sample 15) and (C) cess pit fossil (Sample 17) corncockle seed coats. Peak numbers refer to compounds listed in Table 2. 8.

Peak no:	M+·:	Compound:	Origin:
1	84	(3H)-furan-2-one	PS
2	74?	Hydroxypropanol	PS
3	92	Toluene	P
4	102	Pyruvic acid, methyl ester	PS
5	84	(2H)-furan-3-one	PS
6	96	3-furaldehyde	PS
7	82	2, 4-pentadienal	PS
8	96	2-furaldehyde	PS
9	96	4-methyltetrahydrofuran-3-one	PS
10	116	1-acetoxypropan-2-one	PS
11	96	cyclopent-1-ene-3, 4-dione	PS
12	84	(5H)-furan-2-one	PS
13	96	2-methyl-2-cyclopenten-1-one	PS
14	110	2-acetylfuran	PS
15	98	2, 5-dihydro-5-methylfuran-2-one	PS
16	98	2, 3-dihydro-5-methylfuran-2-one	PS
17	110	5-methyl-2-furaldehyde	PS
18	114	4-hydroxy-5, 6 -dihydro-(2H)-pyran-2-one	PS
19	94	phenol	L
20	112	3-hydroxy-2-methyl-2-cyclopenten-1-one	PS
21	98	2, 4-dihydropyran-3-one	PS
22	112	2-hydroxy-3-methyl-2-cyclopenten-1-one	PS
23	116	4-hydroxymethyl-1, 4-butyrolactone	PS
24	110	2, 3-dimethylcyclopenten-1-one	PS
25	124	5-ethyl-2-furfural	PS
26	108	2-methylphenol	?
27	108	4-methylphenol	?
28	124	guaiacol	L
29	128	2-(propan-2-one)tetrahydrofuran	PS
30	126	3-hydroxy-2-methyl-(4H)-pyran-4-one	PS
31	117?	Phenylacetonitrile?	
32	122	2, 4/6-dimethylphenol	L
33	85	5-hydroxymethyl-2-tetrahydrofuraldehyde-3-one	PS
34	122	4-ethylphenol	L
35	138	methyl-formyl-(4H)-pyran-4-one?	?
36	138	cf. Ralph & Hatfield no. 50 (unknown, 2-acetoxy-5-ethylfuran?)	?
37	138	4-methylguaiacol	L
38	142	3, 5-dihydroxy-2-methyl-(4H)-pyran-4-one	PS
39	110	catechol	?
40	126	5-hydroxymethyl-2-furaldehyde	PS
41	120	4-vinylphenol	L
42	148?	cf. 5-hydroxymethyl-2-tetrahydro-furaldehyde-3-one	PS
43	140	3-methoxycatechol	?
44	132	*cis* 4-propenylphenol?	L
45	152	4-ethylguaiacol	L
46	117	indole	P
47	124	4-methylcatechol	L
48	150	4-vinylguaiacol	L
49	154	2, 6-dimethoxyphenol	L
50	134?	*trans* 4-propenylphenol	
51	162	unknown hexose marker	PS
52	164	eugenol	L

continues

53	166	4-propylguaiacol	L
54	136/152?	4-hydroxyacetophenone + 4-hydroxybenzoic acid methyl ester	L
55	152	vanillin	L
56	164	*cis* isoeugenol	L
57	168	2, 6-dimethoxy-4-methylphenol or 1-(4-hydroxy-3-methoxyphenyl) ethanol	L L
58	166	homovanillin	L
59	166	acetovanillone	L
60	182	vanillic acid methyl ester	L
61	180	guaiacylacetone	L
62	180	2, 6-dimethoxy-4-vinylphenol	L
63	180	cf. Ralph & Hatfield no. 96 (unknown?)	
64	180	propiovanillone	L
65	164	*trans* isoeugenol	L
66	144	1, 6-anhydro-β-D-glucopyranose	PS
67	194	*cis* 2, 6-dimethoxy-4-propenylphenol	L
68	178	*trans* coniferaldehyde	L
69	210	syringylacetone	L
70	210	propiosyringone?	L
71	198	1-(3, 5-dimethoxy-4-hydroxyphenyl) ethanol or syringic acid?	L
72	212	dihydrosinapyl alcohol?	L
73	208	*trans* sinapaldehyde	L
74	181	cf. Ralph & Hatfield 1991 nos. 119 & 120 (3-(3, 5- dimethoxy-4-hydroxyphenyl)-3-oxopropanal &propiosyringone)	L
75	137	cf. Ralph & Hatfield no. 96 (unknown?)	
76	137	cf. trans sinapaldehyde	

Table 2.8. Pyrolysis products of crab apple and corncockle seed coats, and blackberry endocarps analysed from ancient cess pits at St. Saviourgate and Coppergate, York. Products were identified based on their retention times and mass spectra with reference to the literature (Ralph & Hatfield, 1991; Galletti & Bocchini, 1995; Stankiewicz *et al.*, 1997; Boon *et al.*, 1989 and van Bergen *et al.*, 1997a). $M^{+\cdot}$ = the molecular ion, L = product derived from lignin, PS = product derived from polysaccharides, P = product derived from proteins.

(catechins; Galletti, 1991), suggesting that tannins may also be an important component of the seed coats. Furthermore, the "characteristic" lignin markers present in the seed coats, such as guaiacol, might also be derived from pyrolysis of tannins (van Bergen, *pers comm.*, 1999).

The corncockle seed coats appear to have a composition which is dominated by polysaccharides and proteins, with contributions from tannins but with only minor amounts of lignin, if any. Although dicotyledenous seed coats are commonly assumed to comprise ligno-cellulose, the composition of relatively few species has been investigated. Radish seed coats are known to have a predominantly proteinaceous non-polysaccharide component, with minor contributions from ligno-cellulose and an additional unknown polyphenolic biomolecule (van Bergen *et al.*, 1997b). While tannins were proposed as the source of catechol derivatives in the pyrolysates of modern cone scales (Stankiewicz *et al.*, 1997a), and of the fruit wall of the water lily *Nelumbo* (van Bergen *et al*, 1997a), suggesting that these biomolecules may make a more significant contribution to plant tissues than is currently appreciated.

To establish if corncockle seed coats do have a significant proteinaceous component, amino acids were released by acid hydrolysis, derivatised, identified and quantified using GC/MS. Thirteen amino acids were readily identified in the chromatogram derived from the modern corncockle seed coat (Figure 2. 12. & 2. 13.) confirming that proteins must be present.

2. 3. 1. 4. 1. 2. Composition of the fossil corncockle seed coats

The seed coats yielded (Figures 2. 9. (b) & (c)) comparable distributions of pyrolysis products to the modern specimens. There are clear trends in the relative abundance of different compounds in successively older samples. Py-GC/MS is a qualitative technique, which generates thermally

altered products that cannot be used directly to reveal the extent of degradation of the intact molecules. However, research by Flannery *et al.* (1999 & *in press*) has shown that the results generated by pyrolysis-GC/MS are in good agreement with those obtained from qualitative analyses (by HPLC and GC-MS-SIM), at least for the proteins and chitin analysed in their work. Hence, the relative abundances of the various products in pyrograms may provide a reasonably accurate indicator of the amounts of different biomolecules persisting in fossil specimens.

In both of the 16th Century samples (15 & 17), there is a significant decrease in the relative abundance of the polysaccharide pyrolysis products, with the exception of pyruvic acid methyl ester (**4**) which shows a significant increase. There is also a major decrease in the abundance of catechol (**39**). Conversely, there is an increase in the relative abundance of phenol (**19**), 4-methylphenol (**27**), 2, 4-dimethylphenol (**32**), 4-vinylphenol (**41**) and 4-ethylguaiacol (**45**), which dominate the pyrograms. These *relative* increases may be attributed at least partly to the decreases in the abundances of the polysaccharide products. These trends are also observed in the 13th/14th century (11) and 12th/13th century (64) specimens (not shown), although there are only subtle variations in the distribution of pyrolysis products relative to the younger sub-fossil seeds. The reduction in the majority of the polysaccharide pyrolysis products, coupled with the significant increase in pyruvic acid methyl ester (**4**), suggests that some depolymerisation of the polysaccharides has taken place. Similarly, reduction in the relative abundance of catechols may indicate degradation of tannins. However, the overall similarity between the pyrograms of the oldest and youngest fossil seeds suggests that the seed coats could have reached a relatively stable state (biochemical composition) following initial degradation of the polysaccharides, or that decay simply proceeded at different rates in different cess pits.

2. 3. 1. 4. 1. 3. Composition of modern crab apple seed coats

The pyrolysate of a modern crab apple seed coat reveals both polyphenolic and polysaccharide products (Figure 2. 10. (a)). The polyphenol fraction is dominated by phenol **(19)**, 4-methylphenol **(27)** and catechol (1, 2-benzenediol) **(39)**, and the major polysaccharide (cellulose) markers include 2-furaldehyde **(8)**, 1-acetoxypropan-2-one **(10)** and anhydroglucopyranose (levoglucosan) **(66)**. Crab apple seed coats appear to comprise two distinct tissue layers in cross section but these are mechanically inseparable in modern and sub-fossil specimens. The structure and woody appearance of the coats suggests that they are equivalent to testa, which typically comprise lignin and cellulose (van Bergen *et al.*, 1994a), but the composition of crab apple seed coats had not previously been investigated. The pyrolysate of the modern crab apple seed coat is atypical of angiosperm lignified tissues, which are usually dominated by 2-methoxyphenol (guaiacyl) units and 2, 6-dimethoxyphenol (syringyl) units (e. g. Boon *et al.*, 1989; van Bergen *et al.*, 1994a), compounds which make only a minor contribution here. Instead, the pyrolysate is dominated by phenol, 4-ethylphenol and 1, 2-benzenediol, compounds which are typically present in only relatively low abundance in angiosperm lignin.

The relative contributions of guaiacol and syringol units to lignin are known to vary between different taxa (van Bergen *et al.*, 1994a), and even between different tissues of the same species (Boon *et al.*, 1989). However, an unusual lignin chemistry may not be sufficient to explain the minor amounts of syringyl and guaiacyl products in the crab apple seed coat pyrolysate, which is dominated instead by phenols and catechols. Although phenols and 1,2-benzenediols (catechols) have been recognised previously in lignified tissues, their precise origin remains

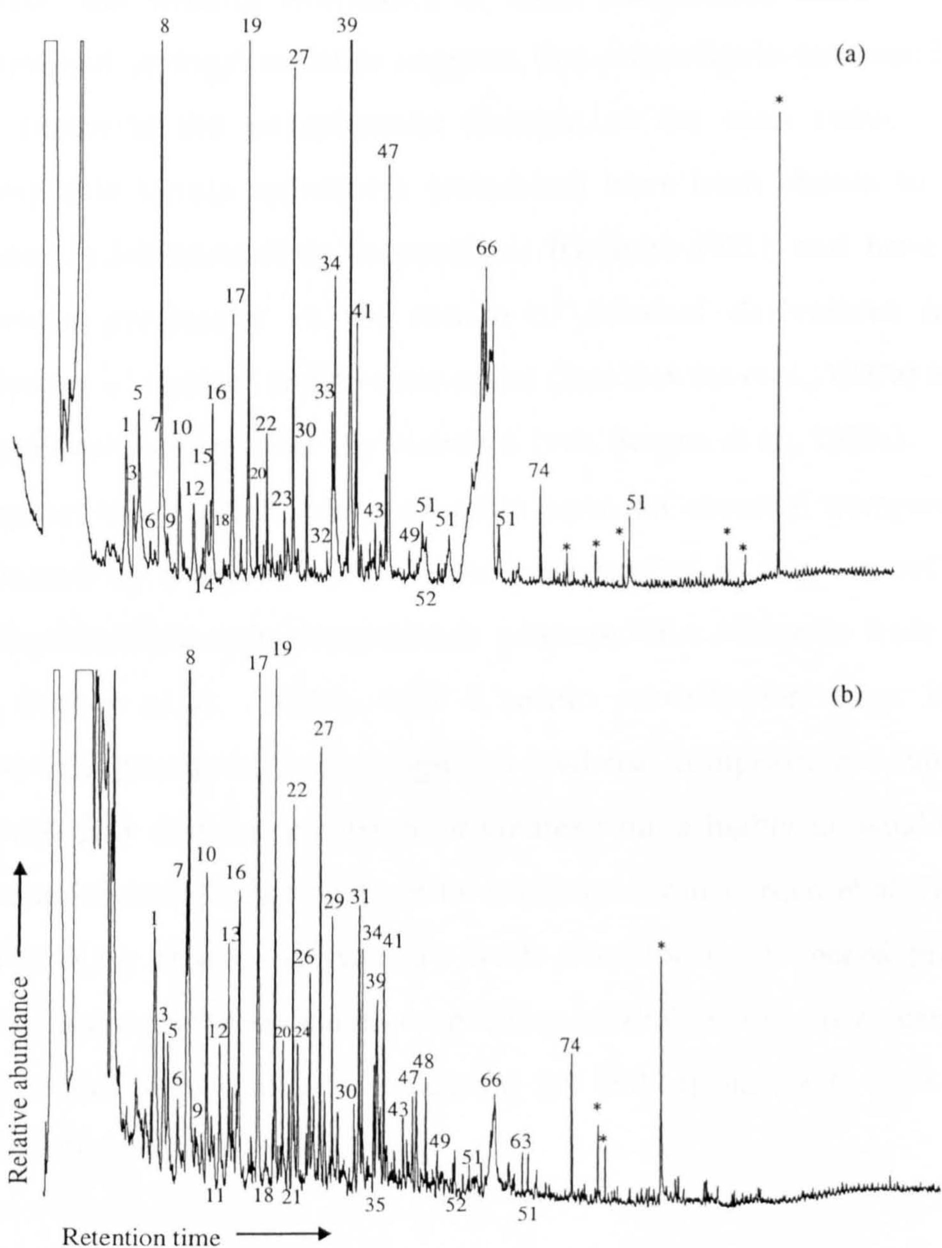


Figure 2.10. Pyrograms (610°C/10s) of (a) modern and (b) Coppergate cess pit sub-fossil crab apple (*Malus sylvestris*) seed coats. Peaks refer to compounds listed in Table 2.8.
* = contaminants (pthalates).

uncertain. Their minor importance in most seeds suggests that they are derived from minor lignin components, although cellulose cannot be excluded as the source (Pouwels *et al.*, 1989). In the crab apple pips, however, the striking abundance of these compounds relative to the guaiacyl and syringyl moieties suggests that a non-lignin macromolecule may dominate the polyphenolic fraction of the seed coats. Non-hydrolysable tannin monomers (catechins) have been shown to yield abundant 1,2-benzenediols on pyrolysis (Galletti, 1991), and have been suggested previously as the source of catechol derivatives in the pyrolysates of modern conifer cone scales (Stankiewicz *et al.*, 1997a) and of the fruit wall of the water lily *Nelumbo* (van Bergen *et al.*, 1997a). Thus, it appears that crab apple seed coats have an unusual composition, dominated by a tannin-cellulose complex similar to the non-cellulose polysaccharide/tannin composition proposed for *Nelumbo* fruit walls (van Bergen *et al.*, 1997a), with a minor contribution from lignin. However, a paucity of data on lignified seed coat composition means that the possibility that the pyrolysate originates from a highly unusual lignin macromolecular structure cannot be excluded. van Bergen *et al.* (1997a) attributed the absence of *Nelumbo* fruits from the fossil record prior to the Holocene to the unusual composition of their walls, so a restricted fossil record would also be predicted for crab apple seeds with their apparently similar composition.

2. 3. 1. 4. 1. 4. Composition of Coppergate crab apple seed coats

The pyrolysate of the Coppergate crab apple seed coat shows a very similar distribution of components to the modern specimen, although there are differences in the relative contributions of the various compounds (Figure 2. 10. (b)). The persistence of the polysaccharide markers (e.g. **8, 17, 22**), and in particular the hemicellulose marker 4-

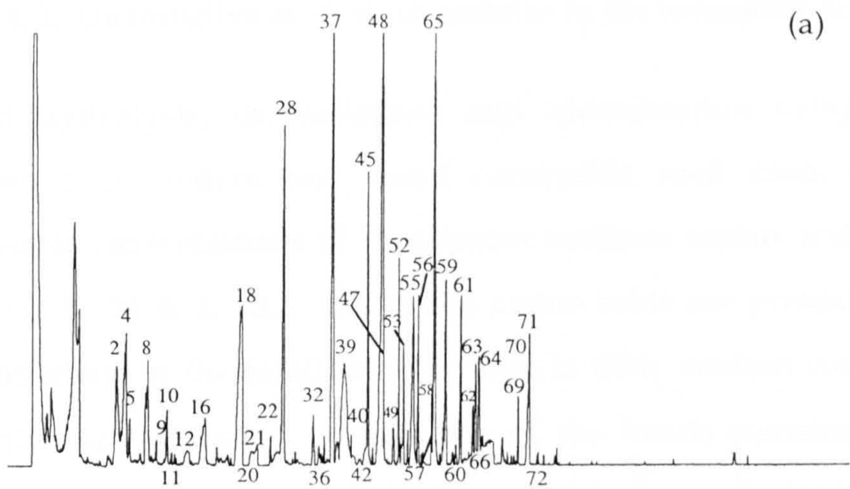
hydroxy-5,6-dihydro-(2H)-pyran-2-one **(18)**, indicates a high level of organic preservation since carbohydrates are the compounds most susceptible to degradation during early diagenesis of woody tissues. The relative increase in the intensity of low molecular weight carbohydrate components, and reduction in that of levoglucosan **(66)**, suggest that minor degradation of cellulose has taken place.

2. 3. 1. 4. 1. 5. Composition of modern blackberry endocarps

Py-GC/MS of a modern blackberry (*Rubus fruticosus*) endocarp reveals polysaccharide and polyphenolic products indicative of a lignocellulose composition (Figure 2. 11. (a); Galletti & Bocchini, 1995; Ralph & Hatfield, 1991; van Bergen et al., 1994a). The pyrolysate is dominated by typical guaiacal (2-methoxyphenol) type lignin markers (**28, 37, 45, 48** and **65**), although syringol markers are also present in lower relative abundances (e.g. **49** and **57**). Polysaccharide products are less abundant overall, being dominated by the hemicellulose (xylan) marker 4-hydroxy-5,6-dihydro-(2H)-pyran-2-one **(18)**. The cellulose markers hydroxypropanol **(2)**, pyruvic acid, methyl ester **(4)**, 2-furaldehyde **(8)**, 1-acetoxypropan-2-one **(10)**, 2,3-dihydro-5-methylfuran-2-one **(16)** and 1,6-anhydro-ß-D-glucopyranose **(66)** are also relatively abundant.

2. 3. 1. 4. 1. 6. Composition of the Coppergate blackberry endocarps

The Coppergate blackberry endocarp yielded a very similar pyrolysate to that of its modern equivalent (Figure 2. 11. (b)). The distribution of lignin and polysaccharide products is largely similar, although a reduction in the relative abundance of the polysaccharide products (e. g. **9** and **10**), and an increase in the relative abundance of others (e. g. **8** and **20**) suggests that degradation of cellulose has occurred. However, the persistence of



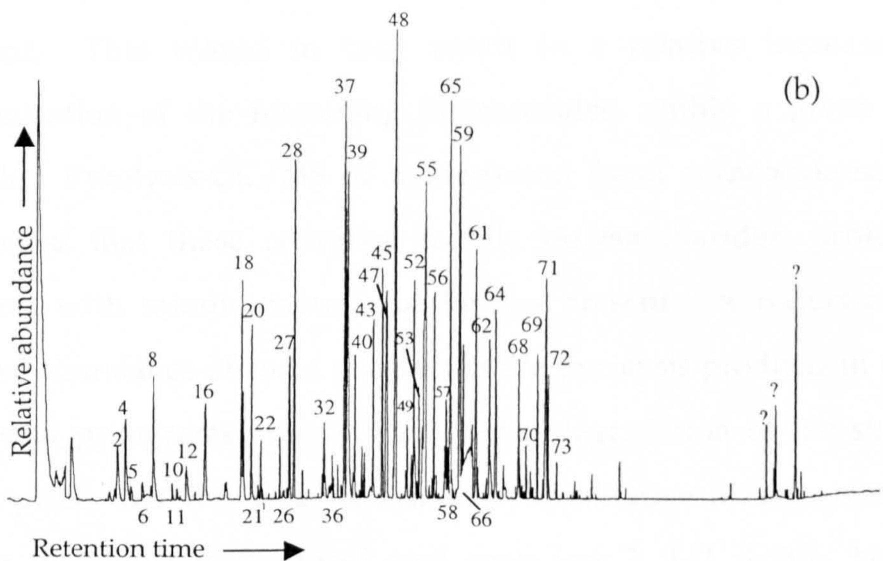


Figure 2.11. Pyrograms (610°C/10secs) of (a) modern and (b) Coppergate cess pit sub-fossil blackberry (*Rubus fruticosus*) endocarps. Peak numbers refer to compounds listed in Table 2.7. ? = unknown compound.

polysaccharide pyrolysis products indicates a high degree of organic preservation similar to that of the Coppergate crab apple seed coats.

2. 3. 1. 4. 2. Quantitative analysis of proteins in the corncockle seed coats

Acid hydrolysis, derivatisation and identification using GC/MS revealed that modern and fossil corncockle seed coats contained appreciable concentrations of 13 different common amino acids (Figures 2. 12. (a) & (b) & 2. 13.). Six of the amino acids are present in lower concentrations in the fossil samples than in their modern counterparts, but with the remainder, at least one of the fossils contains a higher concentration than the modern. Although this seems counterintuitive, it may be explained by partial decay of the seed coats, resulting in a reduction in the amounts of some amino acids and other biomolecules present. This would in turn result in a relative increase in the concentration of the remaining biomolecules, within a given mass of sample. Pyrolysis-GC/MS of modern and fossil corncockle seed coats suggested that these comprise mainly polysaccharides, proteins and tannins, with minor amounts of lignins present. A reduction in the relative abundance of some polysaccharide pyrolysis products in the fossil seed coat pyrograms suggests that some degradation of the sugars has taken place, and this was confirmed by qualitative measurement of the sugars remaining in the fossil seed coats (see 2. 3. 1. 4. 3.). Hence, the higher concentrations of certain amino acids in fossil versus modern corncockle seed coats may be partly explained by a loss of carbohydrates. Degradation of tannins is also a possibility suggested by the lower relative abundances of catechol products present in fossil versus modern seed coat pyrograms.

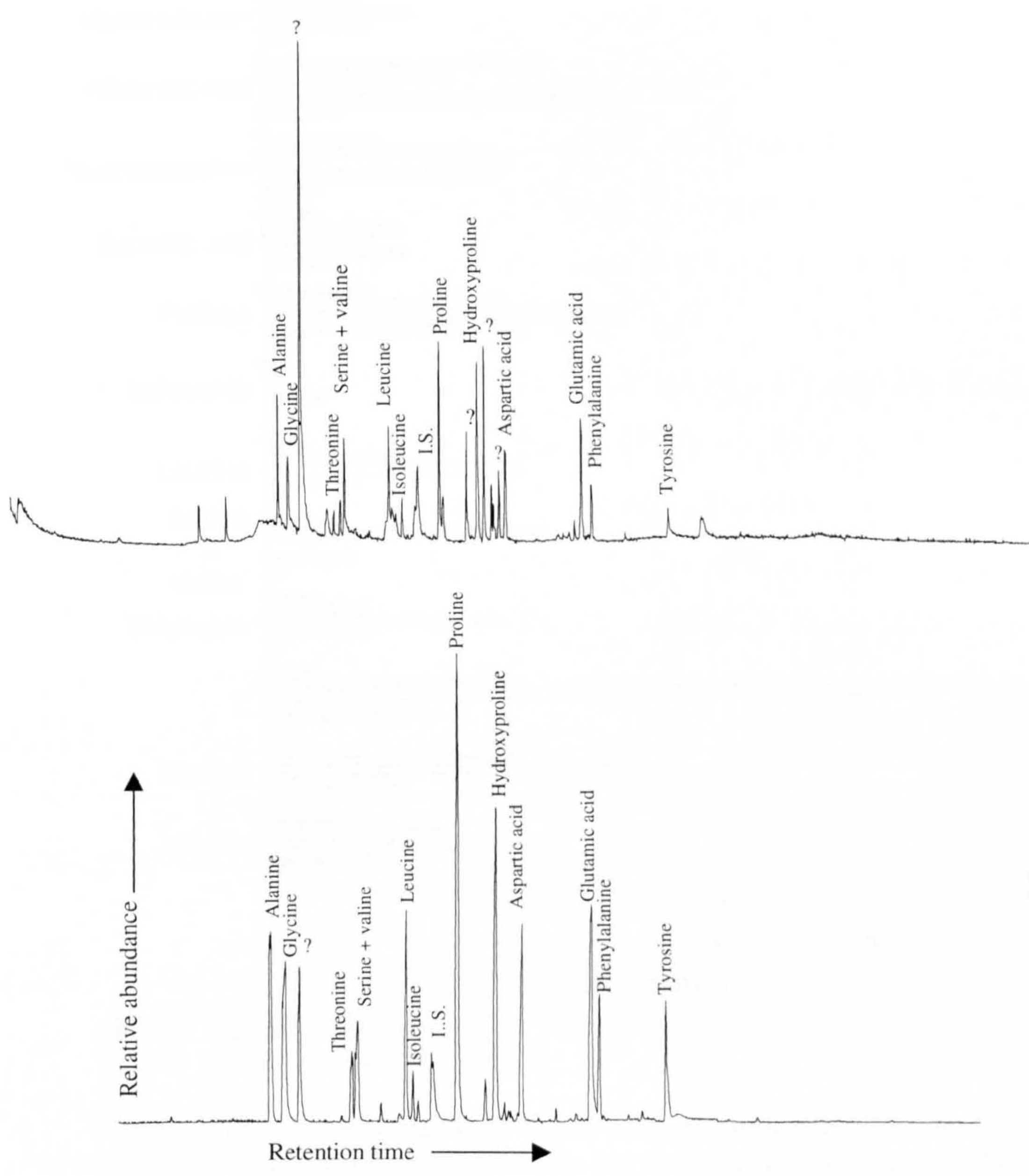


Figure 2.12. Gas chromatograms showing the amino acids detected in the seed coats of (a) modern and (b) cess pit sub-fossil corncockle (*Agrostemma githago*).
I. S. refers to the internal standard (-amino-*n*-butyric acid).

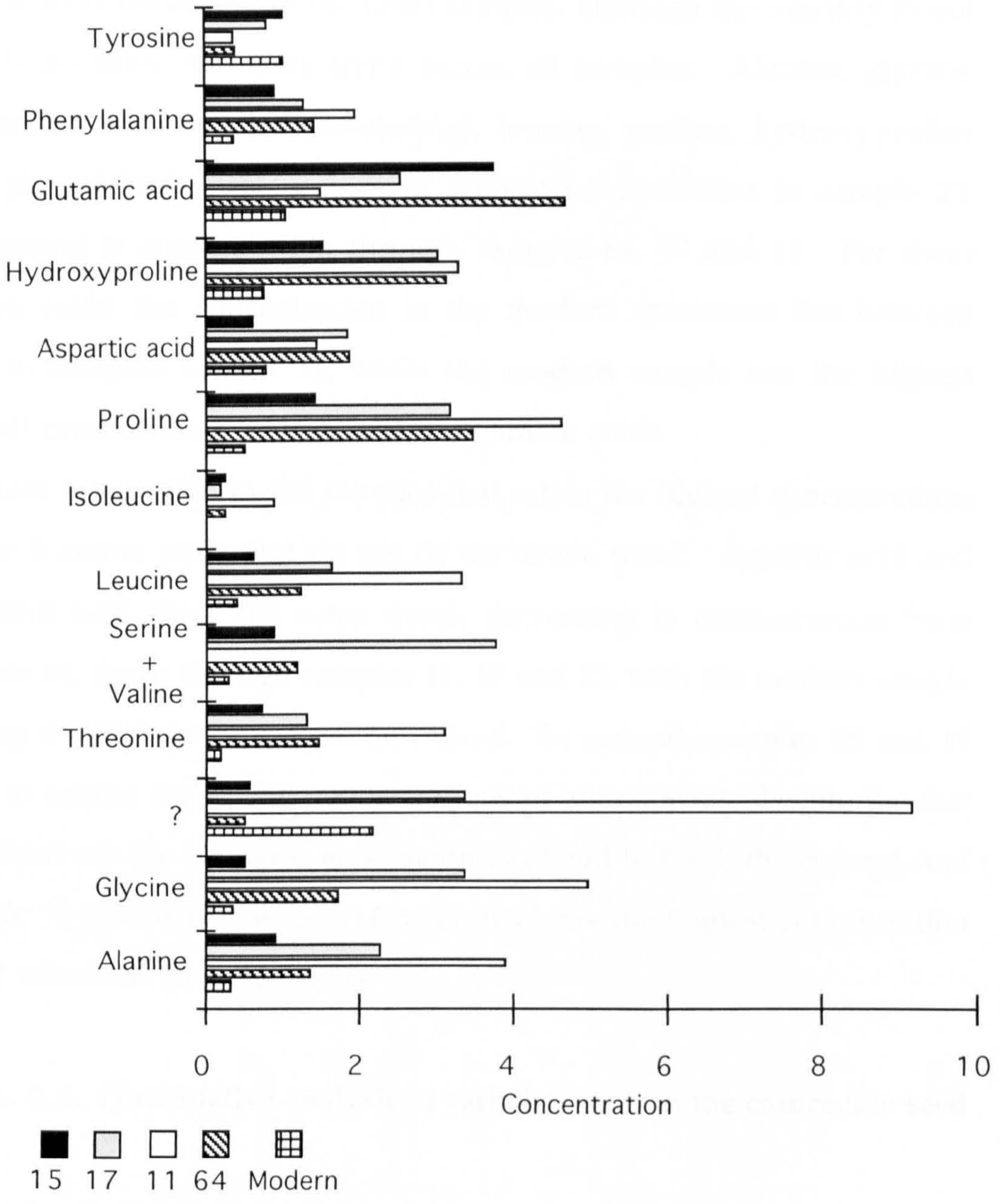


Figure 2. 13. Concentrations of amino acids present in modern and various cess pit sub-fossil corncockle (*Agrostemma githago*) seed coats. Concentrations are expressed relative to the internal standard (y-amino-n-butyril acid; equals 1 on the axis) which has a concentration of 0.061µg/mg dry weight.

There is no one consistent trend in the concentrations of different amino acids remaining in the fossil samples, although the majority (9 out of 13) do show the same trend across all samples. Alanine, glycine, threonine, serine+valine (co-eluting), leucine, proline, hydroxyproline and phenylalanine are present in highest concentration in sample 11, decreasing in concentration through samples 64, 17 and 15. For these amino acids, the concentration in the modern specimens lies between that in samples 64 and 11, while the modern sample has the highest overall concentration of the remaining amino acids.

There is variation in the samples that retain the highest concentrations of the 5 amino acids that do not fit the above trend. Aspartic acid and glutamic acid show the same trend, decreasing in concentration from sample 64, down through samples 11, 17 and 15, with the modern sample having the highest concentration overall. In general, samples 15 and 17 tend to exhibit the lowest concentrations of amino acids, despite the fact that these are the youngest fossil samples (dated to the 16th century), and sample 11 (dated to the 13th-14th century) has the highest concentration for 11 out of the 13 amino acids.

2. 3. 1. 4. 3. Quantitative analysis of carbohydrates in the corncockle seed coats

Acid hydrolysis, derivatisation and identification of the carbohydrate component of the modern and fossil corncockle seed coats revealed the presence of 7 monosaccharides (Figures 2. 14. & 2. 15.). The sugars detected indicate the presence of various hemicelluloses and pectin, as well as cellulose. Xylans, mannans and galactans, three major hemicellulose groups, are suggested by the presence of xylose, mannose and galactose, and these commonly have other sugars as substituents in branching structures, such as arabinose and glucose. Fucose and

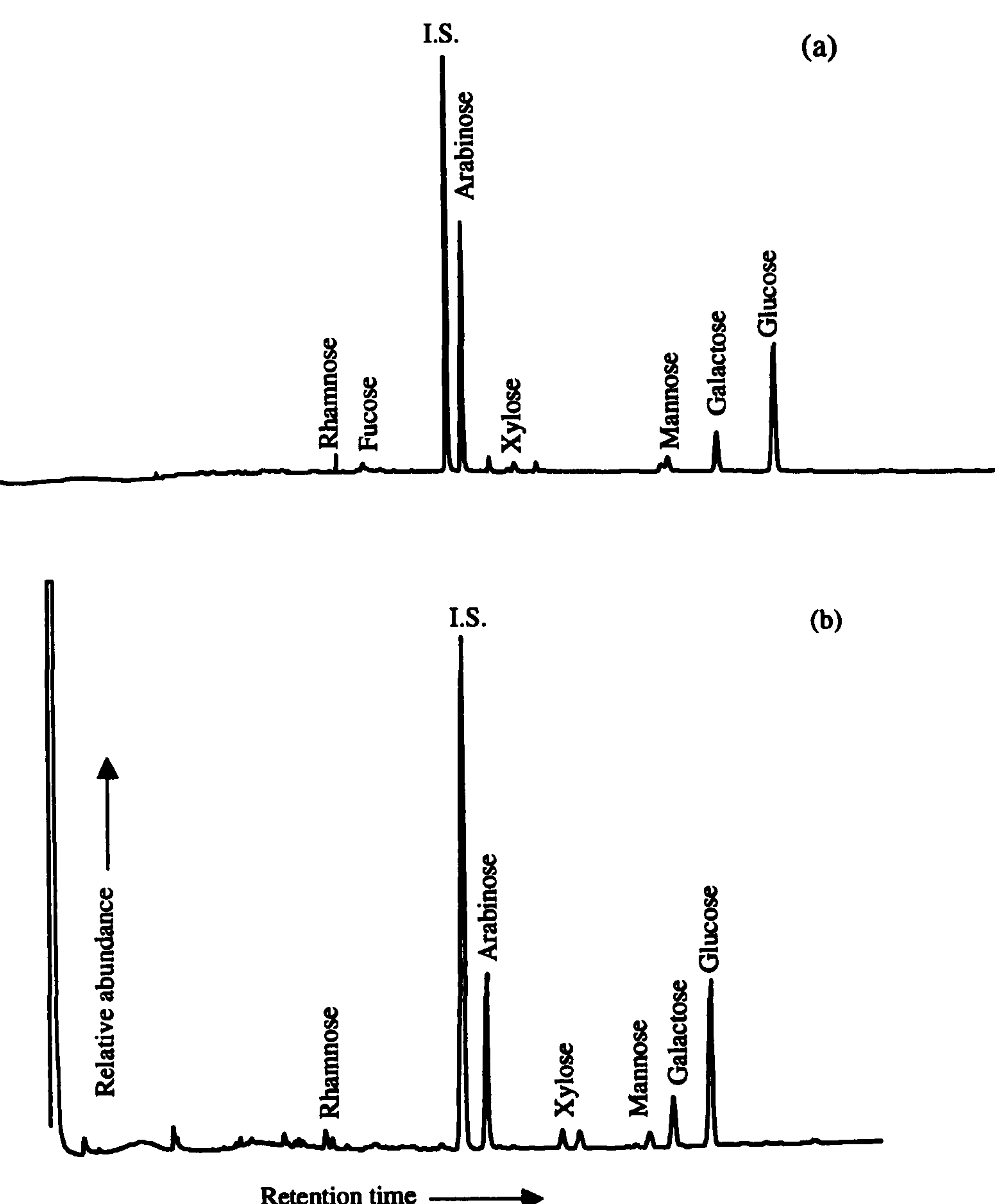


Figure 2.14. Gas chromatograms showing the monosaccharides detected in (a) a modern, and (b) a cess pit sub-fossil corncockle (*Agrostemma githago*) seed coat.

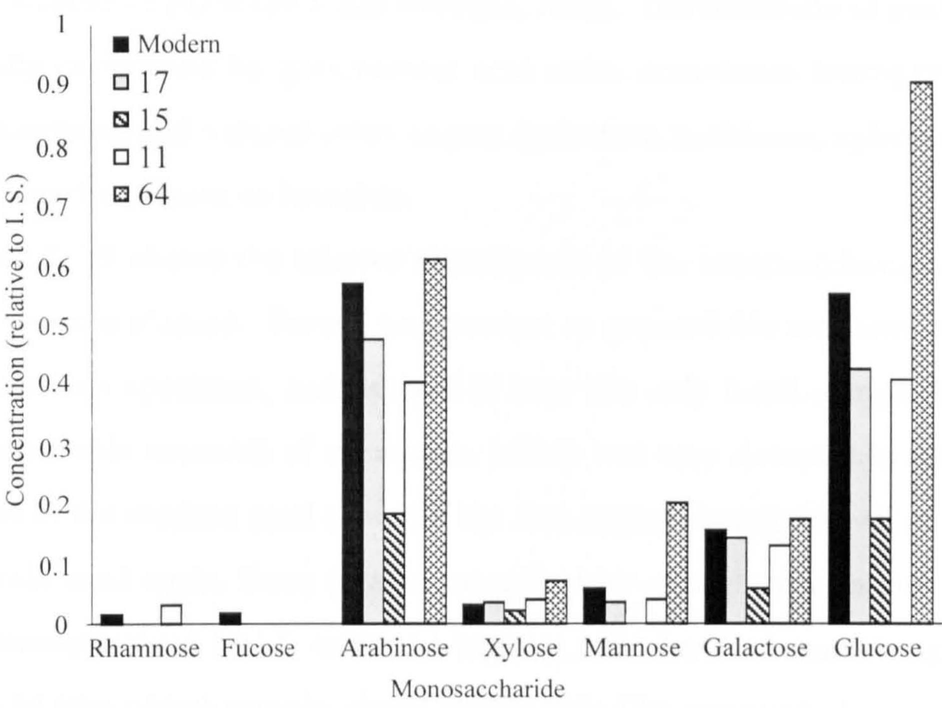


Figure 2. 15. Concentrations of monosaccharides detected in modern and cess pit sub-fossil corncockle (*Agrostemma githago*) seed coats. Concentrations are expressed relative to the internal standard (Pentaerythritol) which has a concentration of 0. 04 μg per mg dry weight.

rhamnose may be found in pectins, the polysaccharides found in the middle lamella of plant cell walls (Hedges, 1990). The backbone of pectins is usually dominated by galacturonic acid units, sometimes interspersed with rhamnose, and various other sugars (galactose, arabinose, xylose and fucose) may be present as branches.

Figure 2. 15. shows the relative abundances of the monosaccharides in all the samples studied. Fucose was present in quantifiable amounts only in the modern specimen, and sample 11 was the only fossil sample that had measurable amounts of rhamnose, which was also detected in small amounts in the modern seed coat. Of the five sugars detected in all of the corncockle seed coats, three (arabinose, galactose and glucose) show the same preservational trend, with the highest concentration remaining in sample 64 (the oldest sample, dated to the 12th-13th century), decreasing through samples 17 (16th century), 11 (13th-14th century) and 15 (16th century). In all of these cases, the concentration of the monsaccharide in modern seed coats lies in between that of samples 17 and 64. Indeed, for those sugars detected in sample 64, the concentration always exceeds that in the modern sample. The concentration of xylose is higher in samples 17, 11 and 64 than in the modern specimen. The presence of higher concentrations of some sugars in the fossil seed coats than in the modern specimen may be explained by a loss of other biomolecules from the seed coats through decay, e. g. other sugars, amino acids or tannins. This would result in a relative increase in the concentration of the remaining sugars in a given mass of sample.

For the other two sugars detected in all of the samples (xylose and mannose), the order of decreasing concentration is sample 64>11> 17>15. However, the concentrations of these sugars in samples 11 and 17 are very similar, so that the overall trends in preservation are fairly consistent for all monosaccharides detected. Age of sample does not appear to have any

correlation with preservation, with the highest concentrations of each sugar consistently detected in the oldest sample (64: 12th-13th century), and the lowest concentrations in one of the two youngest samples (15: 16th century). As expected on such a relatively short time scale, pre-burial treatments and burial environment are likely to be the dominant factors dictating preservational state.

Calculation of correlation coefficients for each pair of sugars revealed that there is a significant correlation between the concentrations of mannose and xylose, glucose and galactose, and glucose and xylose present in the fossils, and a highly significant correlation between the concentrations of galactose and arabinose, and glucose and mannose. These correlations may be explained by the presence of the pairs of sugars as components of the same polysaccharides. Among the hemicelluloses, the mannans may comprise just (1>4)-linked ß-D-mannose units, although some have ß-D-glucose within their backbone, as well as other sugars as branches. Similarly, the xylans comprise (1>4)-linked ß-D-xylose units as their backbone but also commonly contain other sugars , such as glucose and arabinose, on branches. A third group of hemicelluloses, the galactans, may also contain a variety of substituent sugars in addition to galactose. Hence, the correlation between the concentrations of the monosaccharides preserved may result from them having been lost together through hydrolysis during decay of hemicelluloses in which they were common constituents.

The absence of measurable amounts of fucose and rhamnose in many of the fossil samples may be explained by the fact that these sugars were components of pectins, which are highly soluble polysaccharides (Hedges, 1990). Although these are the class of carbohydrates with the highest preservation potential within buried woods, this is attributed to their

protected location within the middle lamella, rather than to any intrinsic chemical stability (Hedges, 1990).

2. 3. 1. 5. Total organic C, H and N in modern and Coppergate crab apple seeds

The percentages of C, H and N in Coppergate crab apple seed coats and embryos relative to modern specimens provide a measure of the degree of degradation (Figure 2. 16.). The Coppergate seed coats show only minor reduction in C and H, and a small increase in the percentage of N present, relative to modern seed coats. Conversely, the Coppergate embryo is significantly depleted in all three elements. These results are consistent with replacement of the embryo tissues with calcium phosphate, and with the high degree of organic preservation revealed by pyrolysis of the seed coats.

2. 3. 2. Arthropods and other invertebrates

2. 3. 2. 1. Macroscopic appearance

The invertebrate fossils recovered from the cess pits comprise various mineralised earthworms, dipteran pupae and woodlice, and non-mineralised beetles and a centipede. Some of the worm-shaped mineralised fossils show the obvious segmentation typical of dipteran pupae (Figure 2. 17. A.). One of the unsegmented specimens, interpreted as an earthworm, clearly represents the head or tail, coming to a point in which there is a star-shaped opening (Figure 2. 17. B.). In many of the specimens, the thin, wrinkled outer mineralised layer has flaked off, revealing a pitted surface underneath (Figure 2. 17. C).

The woodlice fossils typically comprise two or three articulated tergites, with mineralised faecal material cemented on their ventral surfaces

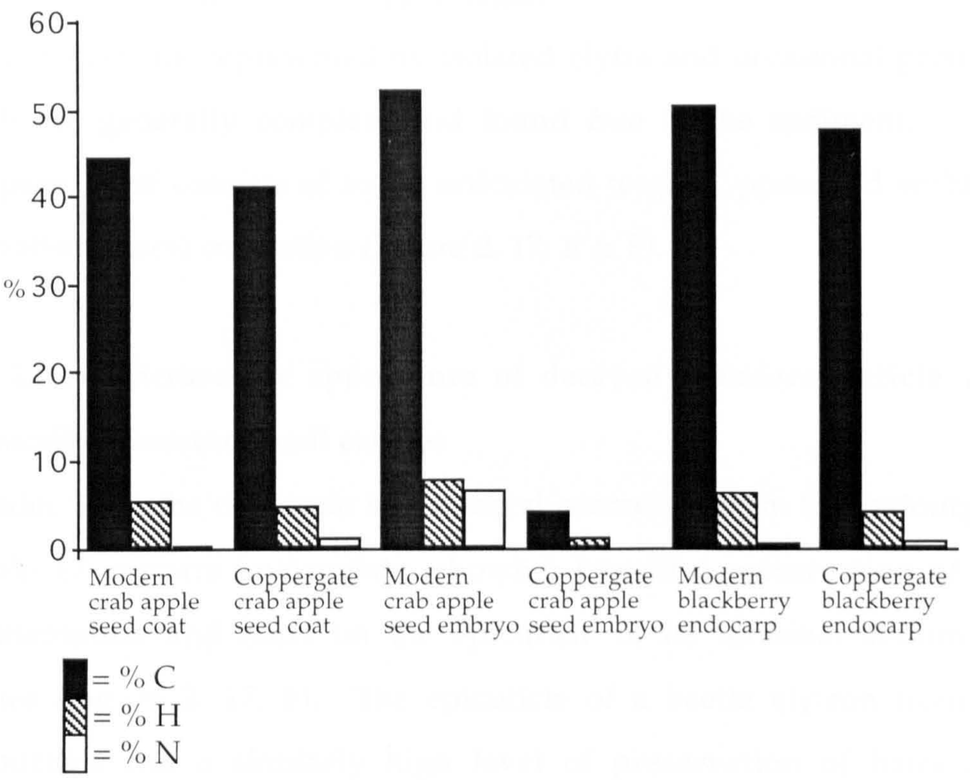


Figure 2. 16. Total organic C, N and H in modern and Coppergate fossil crab apple seed embryos and seed coats, and blackberry endocarps.

(Figure 2. 17. D). Careful removal of this mineralised material from one specimen revealed intact appendages.

The beetles are represented by isolated elytra and occasional pronota, which are generally complete and found free in the sediment. The centipede fossil consists of seven articulated tergites, preserved within a mineralised faecal concretion (Figure 2. 17. E & F).

2. 3. 2. 2. Microscopic appearance of decayed *Manduca* cuticle and organically preserved fossil cuticles

Under SEM, the centipede in the faecal concretion from St. Saviourgate Sample 17 appears immaculate, showing beautiful preservation of the ornamentation and hairs on the epicuticle of its terminal abdominal tergites (Figure 2. 17. F). The epicuticle of a beetle elytron from St. Saviourgate has a similarly high level of preservation of hairs and ornamental processes (Figure 2. 18. A). However, where the procuticle underneath is exposed, this has a fibrous appearance which suggests that some degradation of the proteins which bind the chitin microfibrils together has taken place, leading to their separation (Figure 2. 18. B).

Tergites of fresh *Manduca* cuticle, and of *Manduca* cuticle decayed for 4 weeks and 16 weeks, were prepared for SEM by ripping small sections of cuticle using forceps and then mounting them in various orientations in silver dag on aluminium SEM stubs. The very thin, flimsy nature of the *Manduca* cuticle means that this is very difficult and many sections have to be prepared to obtain usable images under SEM. Using this technique, it was possible to view the endocuticle in some sections. This is the layer underlying the outer cuticle layer, which in fresh *Manduca* sections appears to comprise a meshwork of fibres. During the experimental decay of the mantis shrimp *Neogonodactylus oerstedii*, Stankiewicz *et al.* (1998b)

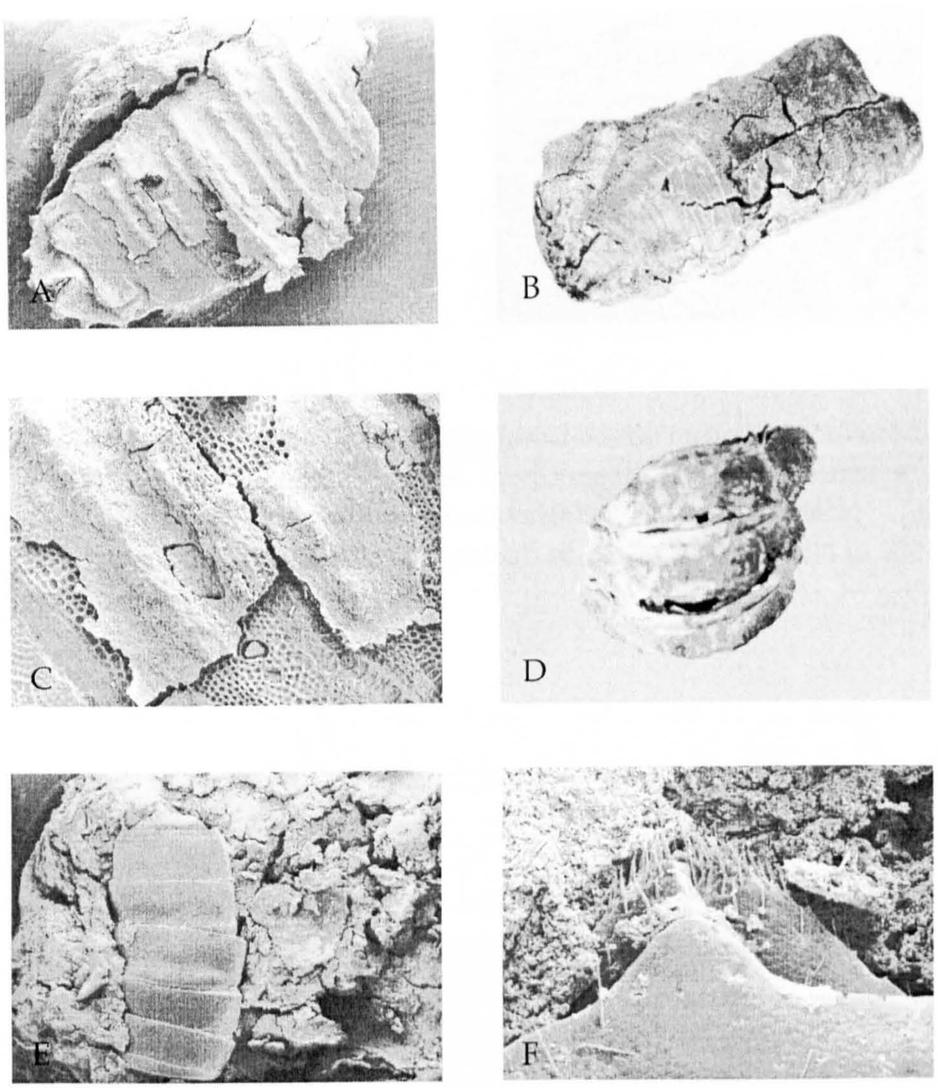
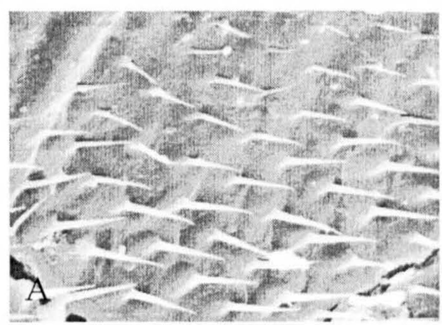


Figure 2. 17. Invertebrate fossils reoovered from archaeological cess pits in York. A. Mineralised dipteran puparium recovered from a 16th Century cess pit at St. Saviourgate (x10). B. Mineralised earthworm from a 16th Century cess pit at St. Saviourgate (x10). C. Surface texture of mineralised dipteran puparium (x50). D. Three tergites of a woodlouse recovered from a 16th Century cess pit at St. Saviourgate (x5). E. Centipede within a mineralised faecal concretion from a 16th Century cess pit at St. Saviourgate (x12). F. Detail of cuticle of centipede in E showng preservation of hairs and surface ornamentation (x150).



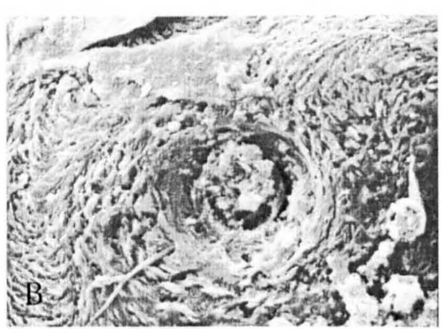


Figure 2. 18. Textures observed in fossil beetle cuticles recovered from 16th Century cess pits at St. Saviourgate, York. A. Surface of beetle epicuticle showing spines (x1000). B. Beetle cuticle showing a pore and subtle separation of chitin microfibrils in the endocuticle (x400).

observed an increase in the size of the gaps between fibres of the endocuticle, as decay advanced. This corresponded to degradation of the protein in between the chitin fibres in the cuticle, making them appear more pronounced, and giving the cuticle an increasingly "stringy" appearance. In the case of the *Manduca* cuticle, no obvious increase in fibre separation was observed in the fresh to 16 weeks decayed specimens. This is unsurprising as pyrolysis generated a very similar distribution of pyrolysis products to the fresh undecayed sample, suggesting that no significant decay of proteins has taken place by this stage. Numerous 32 and 64 week decayed cuticle sections failed to reveal the endocuticle but no obvious degradation was observed in other cuticle layers, again consistent with the pyrolysis data (see 2. 3. 2. 5. 2.).

2. 3. 2. 3. Microscopic appearance of mineralised fossil arthropods, with reference to fresh and decayed modern specimens

A number of mineralised segmented and unsegmented elongate fossils were studied under SEM. One of the segmented fossils clearly represents the posterior end of a dipteran larva or puparium, showing a number of processes around its edge and a triangular groove marking the position of the posterior spiracles (Figure 2. 19. A). The cuticle of the segmented fossils displays two distinct surface ornamentations. The pattern which presumably represents the original structure comprises creased or smooth cuticle, punctuated on each segment by rows of pointed setae running around the circumference of the animals. The five or six setae rows in the modern blowfly *Calliphora* puparia (Figure 2. 19. C) and larvae are present on one of the fossils, but the remainder display just two or three setae rows (Figure 2. 19. B). The creased cuticle present in many of the fossils resembles modern *Calliphora* puparia (pupal cases) more closely

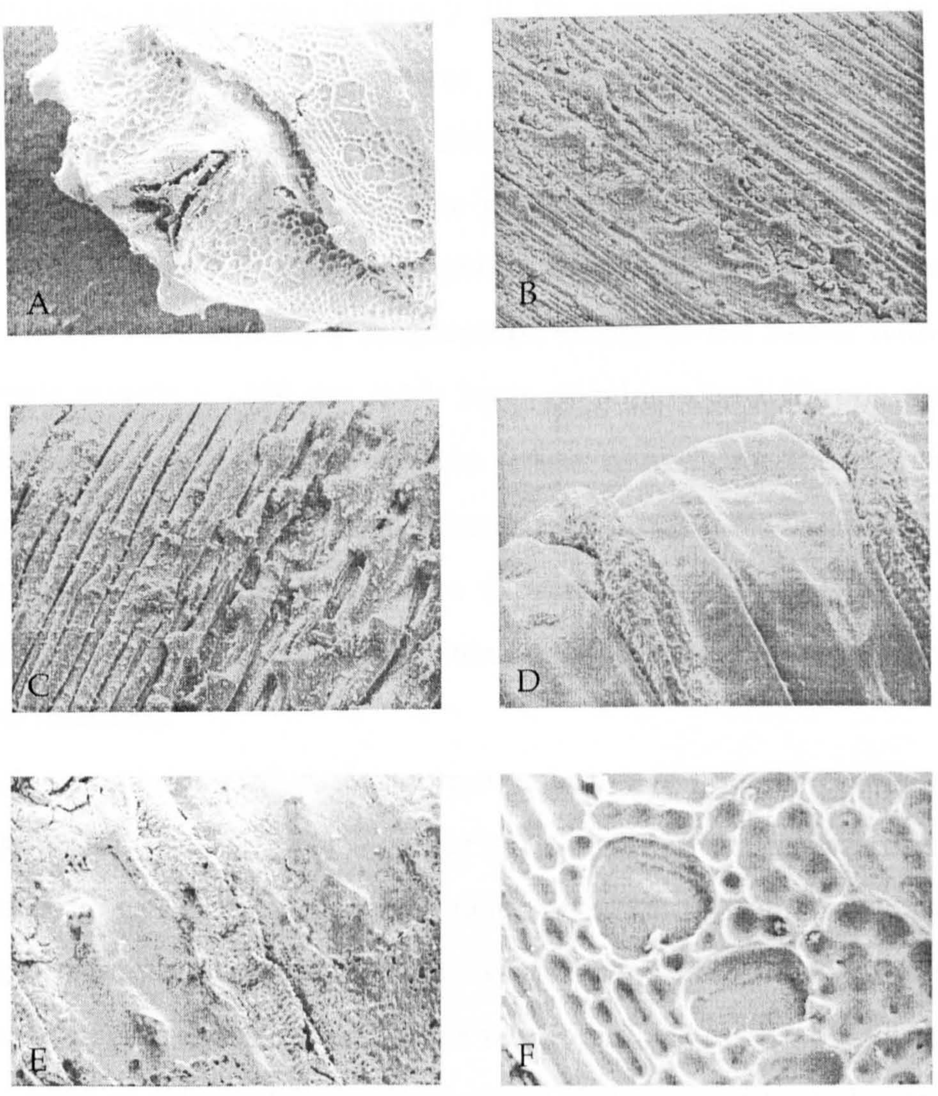


Figure 2. 19. Textures observed in mineralised dipteran puparia recovered from 16th Century cess pits at St. Saviourgate, York. A. Posterior end of puparium showing triangular groove marking the position of the posterior spiracle (x60). B. Cuticle surface of fossil puparium showing two rows of setae (x140). C. Cuticle surface of modern *Calliphora* sp. puparium showing five rows of setae (x140). D. Cuticle of modern *Calliphora* sp. maggot showing smooth surface and bands of setae (x25). E. Ventral surface of fossil maggot showing pro-legs (x10). F. Surface ornamentation of fossil puparia comprising coalescing circular indentations (x220).

than *Calliphora* larvae, suggesting that these represent mineralised puparia rather than larvae. The cuticle of *Calliphora* larvae is smooth but also displays setae rows (Figure 2. 19. D), a condition observed in just one of the fossils. However, creases similar to those observed in puparia cuticle might be produced if shrivelling up of the larvae occurred during fossilisation. Stubs marking the position of prolegs in two specimens provide evidence that at least some of the fossils represent larvae (Figure 2. 19. E). Furthermore, a cross-section of one of the fossils with creased cuticle reveals a ~100 μm thick layer of mineralised fibrous structures, interpreted as transverse muscle tissue underlying the cuticle. This confirms that the fossil is a mineralised larva, as a cross-section of a mineralised puparium would be expected to just reveal the cuticle, or possibly two cuticle layers and then a muscle layer if the pupa inside was also fossilised.

A second type of surface ornamentation is equally common in the segmented fossils, and comprises a dense covering of circular indentations (with a mean diameter of ~10 μm), which often coalesce (Figure 2. 19. F). One specimen clearly shows that this layer is revealed where the overlying creased layer with setae has peeled off (Figure 2. 17. C). SEM of dissected fresh and decayed *Calliphora* larvae failed to reveal a tissue layer with this style of ornamentation, suggesting that it represents a diagenetic artefact. The cuticle surface of *Calliphora* larvae which have been decayed for two weeks has a spotted appearance under the light microscope. SEM reveals that the spots actually consist of densely packed, circular microbial colonies, which often form larger clumps. The indented ornamentation on the mineralised fossils is interpreted as having resulted from mineral precipitation on the surface of the cuticle surrounding microbial colonies like these. The microbes themselves

were not mineralised, creating moulds of their colonies in the mineralised surface once they had decayed.

The non-segmented, elongate mineralised fossils are interpreted as fragments of earthworms, on the basis of comparison with modern specimens. The outer surfaces of these fossils appear less well preserved than the diptera larvae, having a dirtier, more grainy appearance (Figure 2. 20. A) than their modern counterparts. However, setae are usually retained on the surface and the outer epidermis of one specimen has a very fibrous appearance, presumably due to mineralisation of collagen fibres (Figure 2. 20. B). Preservation of the tissues underlying the outer epidermis is generally poor, typically comprising a mineralised mass which lacks structure. However, localised preservation of muscle sarcolemma (Figure 2. 20. C, E & F) and blood vessels (Figure 2. 20. D) was observed in two specimens which were otherwise bereft of structure.

2. 3. 2. 4. Composition of the mineralised fossil arthropods

EDX analysis of the mineralised maggot (Figure 2. 21.) and earthworm fossils revealed that they are composed of calcium phosphate.

2. 3. 2. 5. Composition of the decayed *Manduca sexta* cuticle and organically preserved insect cuticles

2. 3. 2. 5. 1. Composition of a modern weevil elytron cuticle

Pyrolysis-GC/MS of a modern weevil elytron was carried out to provide a fresh, totally non-degraded standard against which to assess the extent of degradation in the cess pit insect cuticles, in particular the beetle elytra. The pyrogram of the modern weevil cuticle (Figure 2. 22. (a)) is very similar to that obtained for a *Tenebrio molitor* (mealworm beetle) elytron pyrolysed by Stankiewicz *et al.* (1996: Figure 2c). The dominant peaks comprise pyrolysis products of both the proteins (indole (**29**), C1-

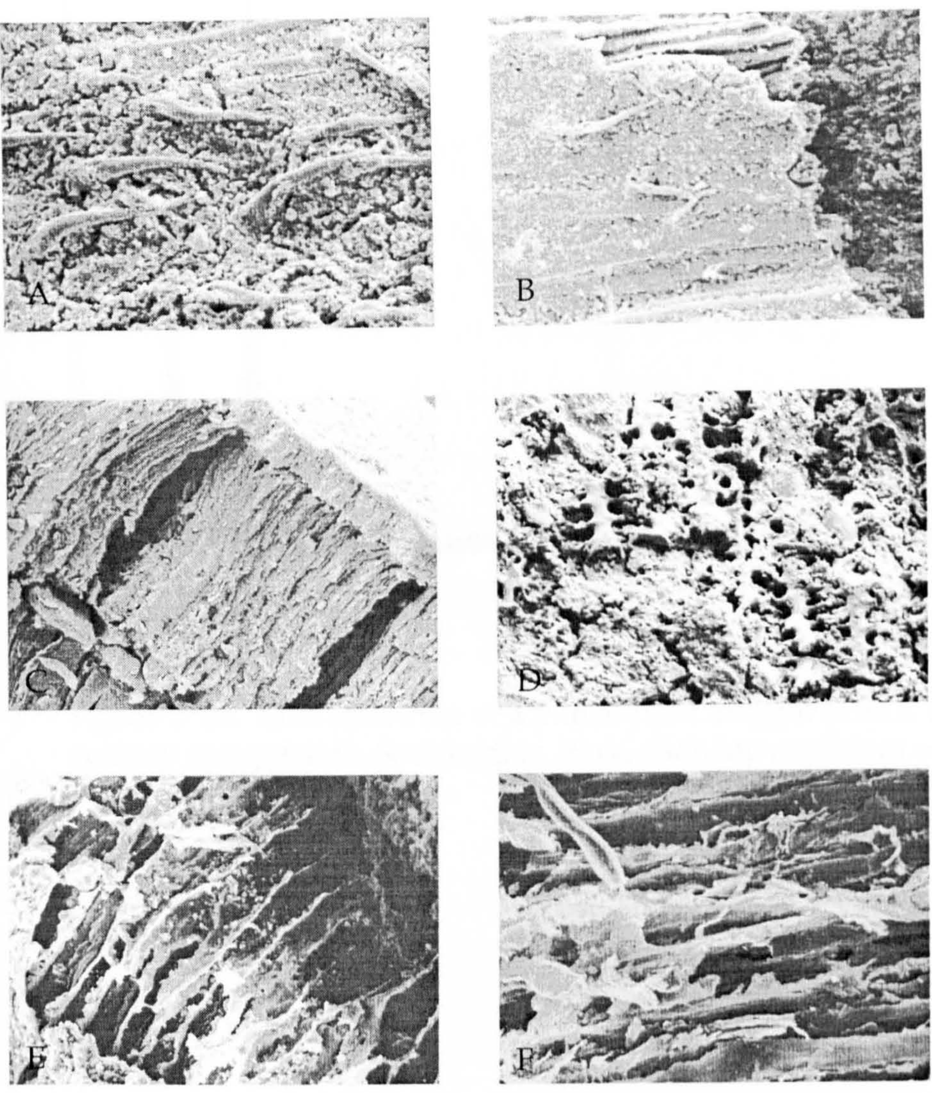


Figure 2.20. Textures preserved in mineralised earthworms recovered from 16th Century cess pits at St. Saviourgate, York. A. Outer surface of mineralised earthworm epidermis showing setae (x 2600). B. Outer surface of mineralised earthworm epidermis showing setae and collagen fibres (x 2600). C. Transverse section through body wall of mineralised earthworm showing a layer of transverse muscle tissue underneath the outer epidermis (x 2850). D. Outer surface of mineralised earthworm showing blood vessels (x 3700). E. Longitudinal section through body wall of mineralised earthworm showing ciircular muscle tissue sarcolemma (x 4300). F. Longitudinal section though the body wall of a modern earthworm showing circular muscle sarcolemma (x 4300).

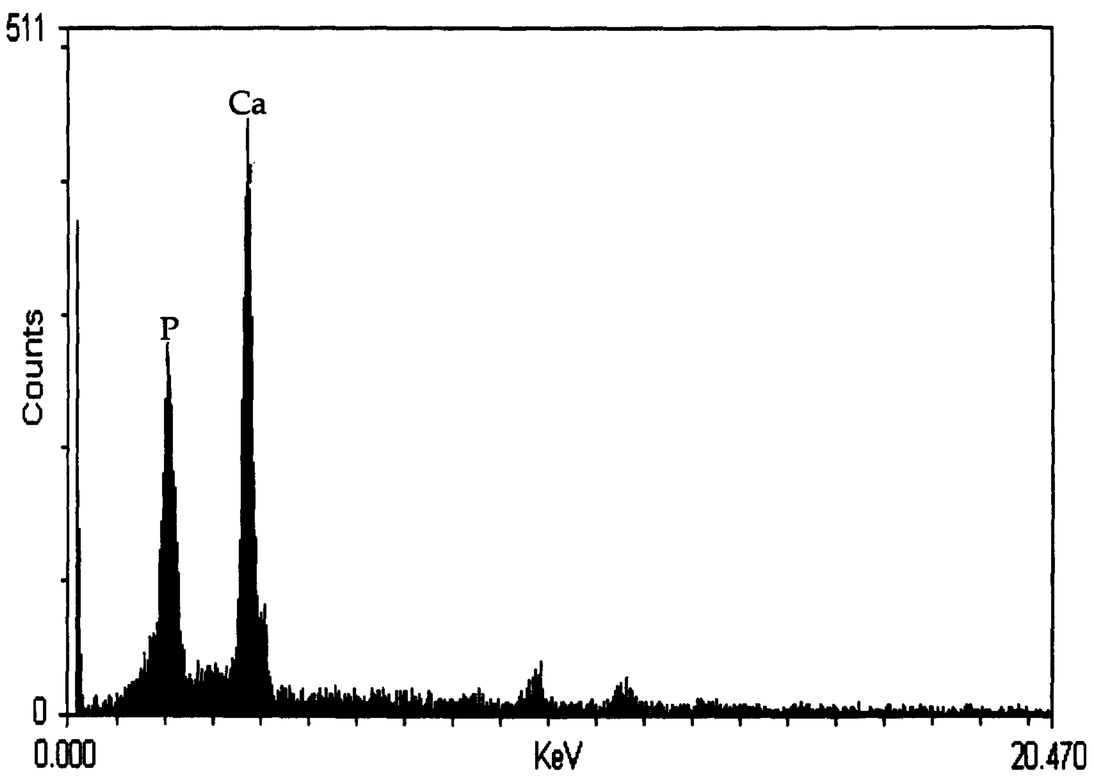


Figure 2. 21. EDX spectrum of a mineralised maggot from a 16th century cess pit at St. Saviourgate, York, showing a calcium phosphate mineralogy.

phenol (**18**) and C_1-indole (**35**)) and chitin (acetamide (**5**), C_1-pyridine (**6**), 3-acetamido-5-methylfuran (**30**), 3-acetamido-4-pyrone (**32**) and oxazoline structures (**37**)) that make up the cuticle.

2. 3. 2. 5. 2. Composition of fresh and decayed horn worm (*Manduca sexta*) cuticle

The pyrolysates of the cuticles of experimentally decayed horn worm pupal exuviae provide a useful reference point against which to assess the extent of degradation of the cuticles recovered from the ancient cess pits. In addition, the fact that the cuticle is from pupal exuviae may make the fresh *Manduca* sample a more satisfactory standard for comparison with the fossil pupal cases than the modern weevil elytron. The analyses also provide some indication of the variation in cuticle composition between different insect taxa.

The chitin/protein composition of the horn worm (*Manduca sexta*) cuticle is typical of arthropods, and similar to that of modern beetles and mantis shrimps (see Stankiewicz *et al.*, 1996, 1997b, 1998b). The pyrogram (Figure 2. 23. (a)) of the fresh *Manduca* cuticle is dominated by the protein markers toluene (**4**), C_1-pyrrole (**8**), phenol (**16**) and methylphenol (**18**), and the chitin products 3-acetamido-5-methylfuran (**30**), 3-acetamido-4-pyrone (**32**) and oxazoline structures (**37**).

Although the pyrograms of fresh cuticle and those of cuticles decayed from 2 to 64 weeks are similar (Figures 2. 23. (b) and 2. 24. (a) to (c)), some variations in the distributions can be recognised. A decrease is observed in the relative abundances of compounds (**5**), (**30**) and (**37**), representing a decrease in the chitin pyrolysis products acetamide, 3-acetamido-5-methylfuran and some of the oxazoline structures. Conversely, there is an increase in the relative abundance of the protein markers phenol (**16**), indole (**29**) and C_1-indole (**35**). More dramatic changes in relative

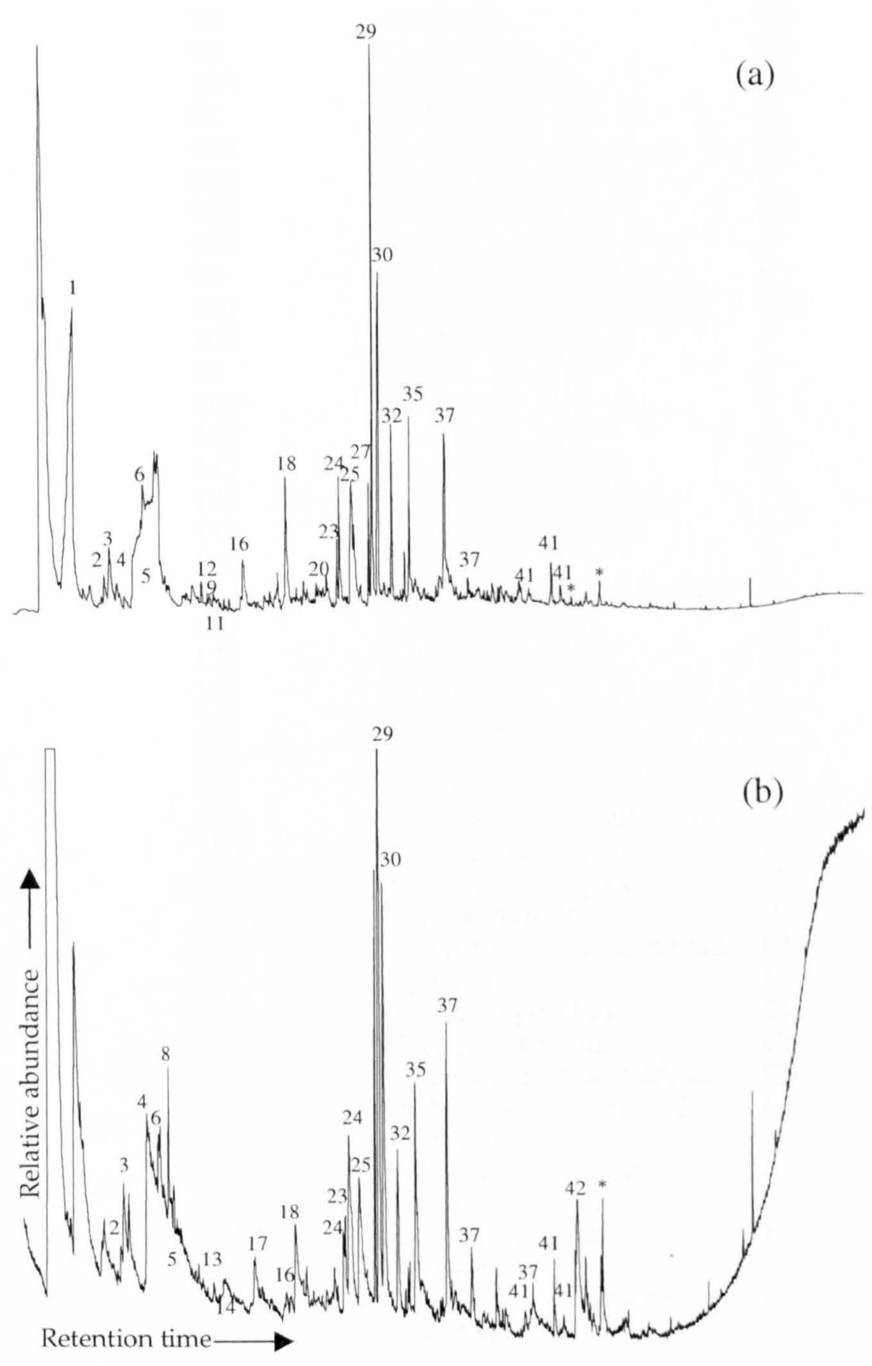
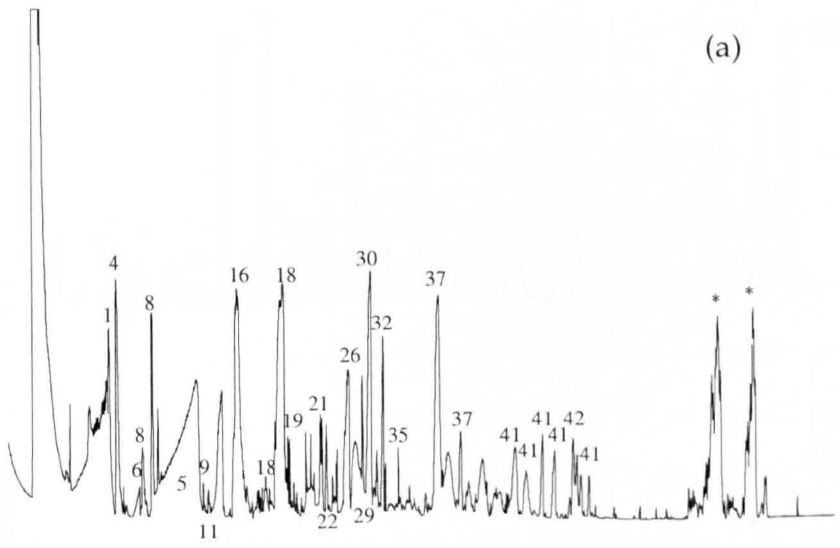


Figure 2. 22. Pyrograms of (a) modern Weevil elytron cuticle and (b) St. Saviourgate cess pit sub-fossil beetle elytron cuticle (Sample 17).

Peak number:	M+·:	Compound:	Source:
1	60	Acetic acid	Ch
2	79	Pyridine	Ch
3	67	Pyrrole	Ch/P
4	92	Toluene	P
5	59	Acetamide	Ch
6	93	C_1-Pyridine	Ch
7	113	Acetylpyrroline	Ch
8	81	C_1-Pyrrole	P
9	107	C_2-Pyridine	Ch
10	106	Ethylbenzene	P
11	109	Acetylpyrrole	Ch
12	104	Styrene	P
13	95	C_2-Pyrrole	P
14	107	2-Pyridinecarboxaldehyde	Ch
15	109	C_3-Pyrrole	P
16	94	Phenol	P
17	109	C_3-Pyrrole	P
18	108	C_1-Phenol	P
19	117	Ethylcyanobenzene	P
20	123	Acetyldihydropyridine	Ch
21	113	C_1-Pyrrolidinedione	P
22	122	C_2-Phenol	P
23	151	2-Pyridinemethanol acetate	Ch
24	137	Acetylpyridone?	Ch
25	125	3-Acetamidofuran	Ch
26	120	Vinylphenol	P
27	152	Catechol acetate	Ca
28	131	Propylcyanobenzene	P
29	117	Indole	P
30	139	3-Acetamido-5-methylfuran	Ch
31	153	3-Acetamido-2-pyrone	Ch
32	153	3-Acetamido-4-pyrone	Ch
33	186	Diketodipyrrole	P
34	151	N-Hydroxyphenylacetamide	Ch
35	131	C_1-Indole	P
36	136	Isobutyl-pyrimidine	Ch
37	185	Oxazoline structure	Ch
38	167	3-Acetamido-5-acetylfuran	Ch
39	185	Diahydro-2-acetamido-2-deoxyglucose	Ch
40	154	Pyrrolidinopiperazine derivative	P
41	168/194	2, 5-diketopiperazine derivative	P
42	204	1, 6-Anhydro-2-acetamido-2-deoxyglucose	Ch

Table 2. 9. Pyrolysis products detected in the pyrolysates (610°C/10 s) of modern and cess pit sub-fossil insect cuticles. Peak numbers refer to those used to label the pyrograms. P = product derived from proteins, Ch = product derived from chitin, Ca = product derived from catechol.



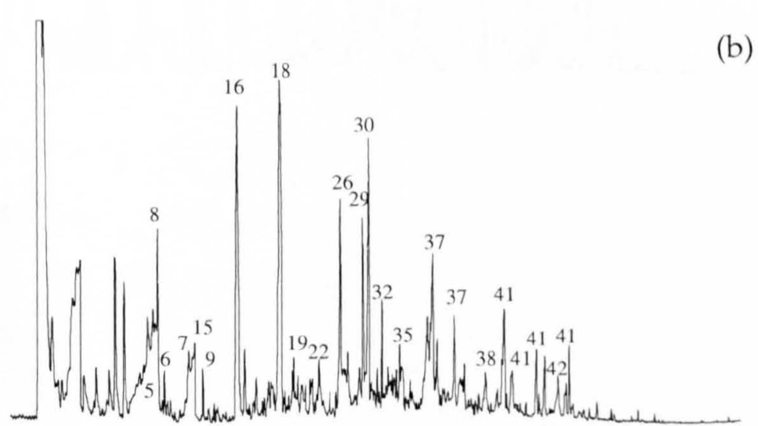
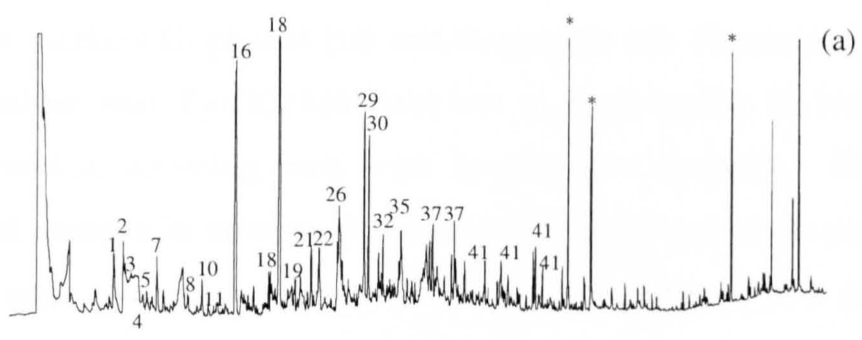
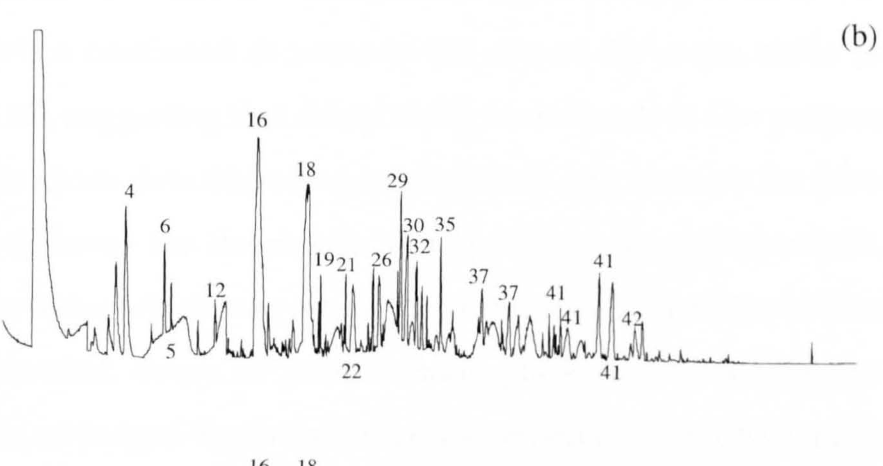


Figure 2. 23. Pyrograms (610°C/10 s) of the cuticle of *Manduca sexta*, (a) fresh and (b) decayed in the laboratory for 2 weeks. Peak numbers refer to compounds listed in Table 2. 9. * = contaminants (pthalates).





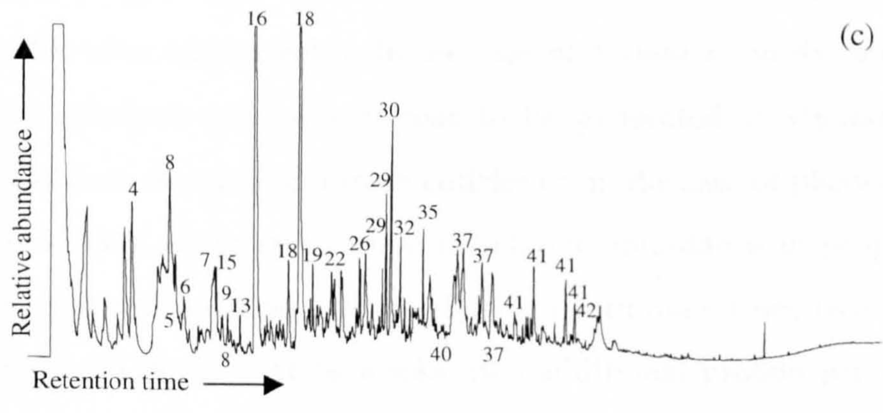


Figure 2. 24. Pyrograms of cuticle of *Manduca sexta* decayed for (a) 16 weeks, (b) 32 weeks and (c) 64 weeks. Peak numbers refer to compounds listed in Table 2. 9. * = contaminants (pthalates).

abundance are apparent in the pyrogram for *Manduca* cuticle decayed for 64 weeks (Figure 2. 24. (c)). Relative to the 32 weeks decayed cuticle pyrogram, there is a marked increase in the relative abundance of the protein markers C_1-phenol **(18)** and C_1-pyrrole **(8)**. Flannery *et al.* (1999) established that Py-GC/MS data are a good guide to biomolecule preservation, agreeing well with quantitative analysis. Hence, the marked changes in relative abundances of protein pyrolysis products in the 64 week pyrogram suggest that protein degradation is now proceeding at a faster rate than in earlier decay samples, generating a greater proportion of these low molecular weight decay products. In addition, there is a continued decrease in the size of the major chitin (acetamide) peak **(5)**, suggesting that decay of this biomolecule is also progressing.

The above data indicate a much slower rate of decay for *Manduca* than that observed for the mantis shrimp *Neogonodactylus oerstedii,* decayed in sea water which was anaerobic at the outset (Stankiewicz *et al.,* 1998b). In this case, decay of proteins took place rapidly within the first few weeks, as judged by the fact that few amino acid pyrolysis products were detectable after eight weeks. In the case of *Manduca,* on the other hand, protein pyrolysis products appear to be generated in similar relative abundances in decayed and fresh cuticles or, in the case of phenol **(16)** and C_1-indole **(35)**, show an increase in relative abundance in progressively longer decayed specimens, a trend which continues from two to thirty-two weeks of decay. At 64 weeks, two additional protein products (C_1-phenol **(18)** and C_1-pyrrole **(8)**) show an increase in relative abundance, while C_1-indole has decreased in relative abundance, suggesting the onset of more significant protein degradation. The observed increase of some protein markers, particularly at the low molecular weight end of the pyrogram, and the decrease in C_1-indole by 64 weeks, suggests decay of the protein in the cuticle. The decrease in relative abundance of some chitin

pyrolysis products, and the relative increase in some protein markers is consistent with that observed during *Neogonodactylus* decay, where these products initially increased to dominate the pyrolysate before decreasing again by eight weeks of decay. Even though significant protein decay appears to have yet to take place, this suggests that chitin degradation has begun.

The relatively slow rate of decay observed in the *Manduca* cuticles is consistent with that of beetle cuticles decayed in a freshwater pond by Duncan (1997). Decay of the beetle cuticle proceeded much more slowly than that of *Neogonodactylus* under marine conditions (Stankiewicz *et al.*, 1998b), with all protein and chitin pyrolysis markers still detectable after 30 weeks in the pond. However, more significant reduction in the amounts of protein moieties present in the beetle cuticle pyrolysate was observed after 30 weeks, by which stage it was dominated by chitin products. The *Manduca* cuticles had apparently reached a less advanced state of decay by week 64, with protein moieties showing the first evidence of decreasing in relative abundance in the pyrogram. This may be due to the presence of a more diverse assemblage of decay organisms in the natural freshwater setting than in the *Manduca* laboratory decay vessels.

2. 3. 2. 5. 3. Composition of a modern dipteran (*Musca* sp.) pupal case

The pyrolysate (Figure 2. 25. (a)) of a modern *Musca* sp. pupal case is dominated by chitin products such as acetamide **(5)**, acetylpyridone **(24)**, 3-acetamido-5-methylfuran **(30)**, N-hydroxyphenylacetamide **(34)** and 3-acetamido-5-acetylfuran **(38)**, although some protein moities are also present in relatively high abundances: pyrrole **(3)**, phenol **(16)**, C_1-phenol **(18)** and 2, 5-diketopiperazines **(41)** (derived from dipeptides). Most protein markers (including C_1-pyrroles **(8)**, ethylbenzene **(10)** and styrene

(12)) are present in low abundances relative to those of the chitin products. The largest peak in the pyrolysate is the combined pyrrole/acetamide peak (3/5).

2. 3. 2. 5. 4. Composition of a St. Saviourgate dipteran pupal case (sample 17)

This fossil pupal case was recovered from a different 16th Century cess pit sample than sample 15 discussed above, and the two cuticle specimens yielded quite different pyrograms (Figures 2. 25. (b)), although chitin and protein products still persist in both. This pupal case pyrogram is dominated by a number of chitin products, including 3-acetamido-5-methylfuran (30), 3-acetamido-4-pyrone (32) and oxazoline structures (37), although protein markers such as phenol (16), C_1-phenol (18) and C_1-indole (35) are also relatively abundant.

The sample 17 pupal case pyrolysate is very similar to that of the modern *Musca* pupal case, with the chitin and protein products present in similar relative abundances. However, some degradation of the fossil sample is suggested by the reduction in the size of the pyrrole/acetamide peak (3/5) and a relative increase in the size of the 3-acetamido-5-methylfuran (30) peak. In terms of the cuticles of the *Tenebrio* mealworm beetle decayed for various time periods under natural freshwater conditions (Duncan, 1997), the sample 17 fossil pupal case probably corresponds most closely to less than 2 weeks of decay, as significant reduction in the protein moieties has yet to take place.

Due to differences in cuticle composition between different structures and taxa (Stankiewicz *et al.*, 1996), it is more difficult to assess the extent of degradation of the pupal case relative to the *Manduca* cuticles decayed in the laboratory. The relative abundances of protein products such as

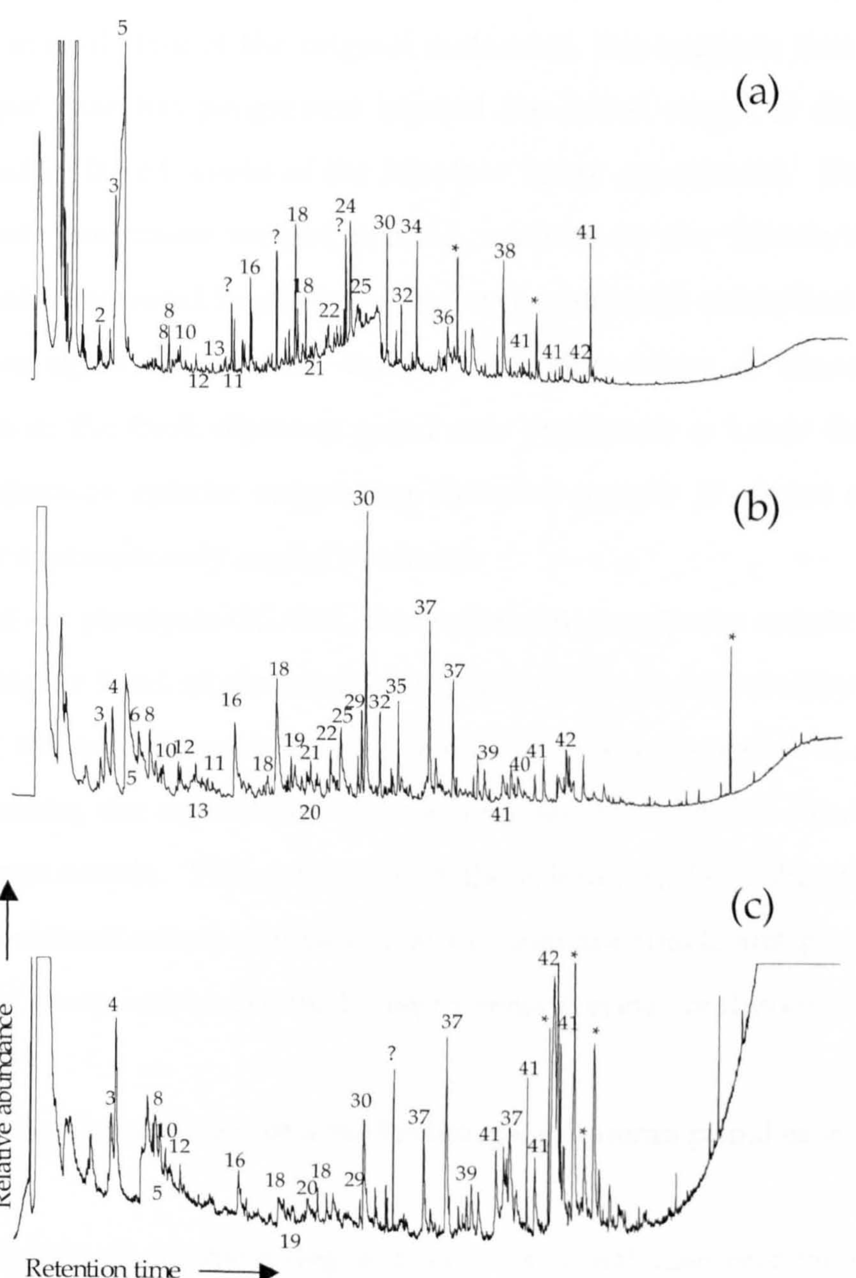


Figure 2. 25. Pyrograms of dipteran pupal case cuticle. (a) Modern *Musca* sp pupal case and sub-fossil pupal cases from (b) cess pit Sample 17 and (C) cess pit Sample 15 at St. Saviourgate, York.

phenol (16) and C_1-phenol (18) in the pupal case pyrolysate are significantly lower than in the fresh *Manduca* cuticle. If relative abundances of pyrolysis markers is taken as an indicator of relative preservational state of the original molecules, this suggests that decay of the pupal case has progressed beyond the initial stages of degradation observed in the 64 weeks of the *Manduca* decay experiment. During this time, low molecular weight protein markers in the *Manduca* cuticle pyrolysates increased in relative abundance, and by 64 weeks had begun to decrease again. However, the relative abundance of these protein markers in the fresh dipteran pupal case pyrolysate is lower than in the fresh *Manduca* cuticle, suggesting that the sample 17 pupal case may actually represent only negligible decay.

Based on pyrolysis-GC/MS, this sub-fossil pupal case cuticle shows a much higher level of chemical preservation than the laboratory-decayed mantis shrimp *Neogonodactylus oerstedii* (Stankiewicz *et al.*, 1998b), representing the equivalent of only one week or less of decay of the crustacean cuticle. This reflects both the sclerotised (and therefore more decay resistant) nature of insect versus crustacean cuticle and possibly also a slower decay rate under freshwater versus marine conditions.

2. 3. 2. 5. 5. Composition of a St. Saviourgate dipteran pupal case (sample 15)

The extent of chemical degradation of a pupal case recovered from a 16th Century cess pit at St. Saviourgate can be best assessed through comparison with the modern dipteran (*Musca* sp.) pupal case, although the cuticles of modern weevil, and fresh and decayed *Manduca* pupal exuviae are also informative. The fossil pupal case pyrogram (Figure 2. 25. (c) comprises a range of compounds derived from both protein and chitin, revealing that both biomolecules are still present. Although the

modern *Musca* sp. pupal case pyrolysate is dominated by chitin products versus those derived from proteins, this pattern is more marked in the fossil pupal case pyrolysate, where protein moities such as C_1-phenol **(18)** and phenol **(16)** are present at much lower relative abundances. The pyrrole/acetamide **(3/5)** peak which dominates the modern pupal case pyrolysate is significantly reduced, although 2, 5-diketopiperazines **(41)** derived from dipeptides persist at relatively high abundances. The major products in the fossil pyrolysate are 3-acetamido-5-methylfuran **(30)** and oxazoline structures **(37)**, along with 1, 6-anhydro-2-acetamido-2-deoxyglucose **(42)**.

The fresh cuticles of both the weevil and *Manduca* yielded pyrolysates that are dominated by a mixture of both protein and chitin products, while that of the fossil pupal case cuticle is biased towards chitin products. Protein products do persist in the fossil pupal case cuticle, but generally in much lower relative abundances than in the fresh cuticle pyrolysates.

It is useful to compare the pupal case pyrolysate to that for the *Manduca* and *Tenebrio* cuticles decayed for various periods of time, to establish whether the pupal case represents an equivalent or more advanced stage of degradation. To do this, it has to be assumed that relative abundances of pyrolysis products are good indicators of biomolecule preservation, an idea supported by the work of Flannery *et al.* (1999).

The low abundance of protein products, such as phenol **(16)** and C_1-phenol **(18)**, relative to chitin products in the fossil pupal case pyrolysate suggests that decay has progressed beyond that observed in even the most degraded (64 week) *Manduca* cuticle. In the laboratory decayed *Manduca* samples, the relative abundance of various protein products (including phenol and C_1-phenol) initially increased in samples decayed for progressively longer periods of time. In the 64 weeks decayed sample

pyrolysate, a slight decrease in relative abundance of these protein products was evident. The initial increase in yield of low molecular weight pyrolysis products presumably reflects the break-up (depolymerisation) of the protein structure into smaller units, resulting in the generation of more low molecular weight products by pyrolysis. Once these smaller units start to decay significantly, the relative abundance of all protein pyrolysis products will begin to decrease. The fossil pupal case cuticle is interpreted as having reached a more advanced state of decay than the longest decayed *Manduca* cuticle, based on a significant reduction in the relative amounts of certain protein products generated by pyrolysis. This stage is roughly equivalent to that observed between 2 and 30 weeks of decay of *Tenebrio molitor* decayed in a natural freshwater setting.

The fossil pupal case has reached a much less advanced state of decay than the mantis shrimp *Neogonodactylus oerstedii* (Stankiewicz *et al.*, 1998b) that had been decayed for just one week in marine conditions. At this stage in laboratory decay of the shrimp, protein products such as toluene and 2, 5-diketopiperazines persisted in relatively high abundances (before decreasing to barely detectable amounts by 2 weeks of decay), and the oxazoline derivatives of chitin had increased in relative abundance to be among the most abundant pyrolysis products. The relatively limited state of decay of the cess pit pupal case and the decayed *Manduca sexta* and *Tenebrio molitor* cuticles, as judged by detection of the full range of pyrolysis products, may be explained by the fact that the mantis shrimp represents crustacean cuticle decayed in anaerobic, marine conditions, whereas decay of insect cuticles under initially aerobic, fresh water conditions proceeds much more slowly. It is likely that the sclerotised nature of the insect cuticles confers on them a much greater

decay resistance than that of the crustacea, whose non-sclerotised cuticles also contain a significant mineral component.

2. 3. 2. 5. 6. Composition of a St. Saviourgate beetle elytron (sample 17)

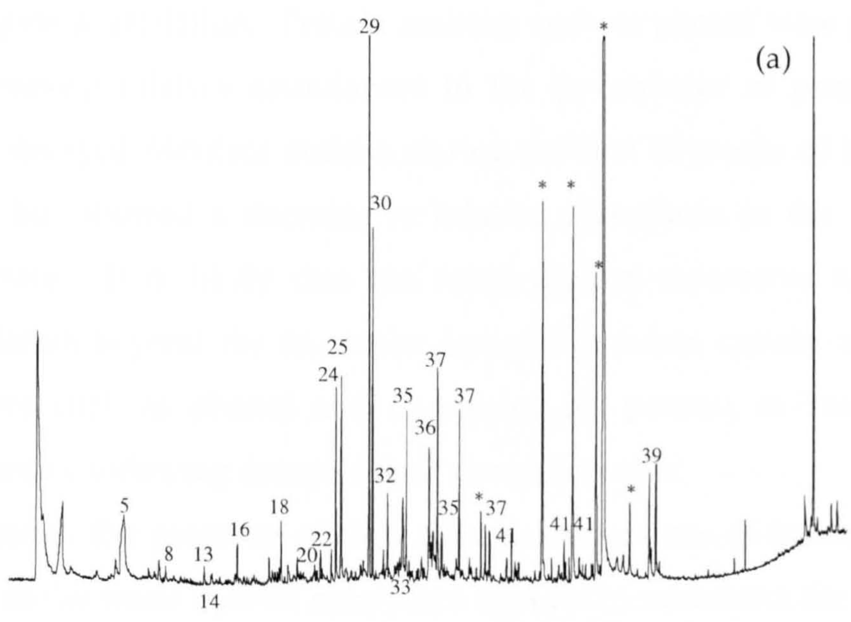
This beetle elytron (sample 17; Figure 2. 22. (b)), recovered from a 16th century cess pit at St. Saviourgate, yielded a pyrolysate comprising a similar range of products to both the modern weevil cuticle (Figure 2. 22. (a)) and the mealworm beetle (*Tenebrio molitor*) cuticle analysed by Stankiewicz *et al.* (1996) and Duncan (1997) respectively. Both protein and chitin products persist and, although the latter generally dominate the pyrolysate, the most abundant product is indole **(29)**, derived from the amino acid tryptophan, a protein marker which also dominates the pyrolysates of the two modern beetle cuticles. However, the relative abundances of some of the other protein markers (e. g. phenol **(16)** and C_1-phenol **(18)**) are lower in the fossil elytron pyrolysate than in both those of the fresh beetle cuticles, suggesting some degradation of the cuticle proteins in the fossil. The stage of decay reached by the fossil elytron is similar to that reached by the mealworm beetle (*Tenebrio molitor*; Duncan, 1997) after 30 weeks of decay in a freshwater pond; the majority of protein moieties have reduced in relative abundance but all are still generated in detectable concentrations by pyrolysis.

Indole is a less important constituent in the cuticle of *Manduca*. Its relative abundance in the *Manduca* specimens altered very little in 64 weeks of decay, suggesting that the amino acid tryptophan from which it is derived represents a relatively decay-resistant component of the protein in insect cuticle. Indeed, this is one of the protein products that persisted to 8 weeks of decay in the mantis shrimp *Neogonodactylus oerstedii* (Stankiewicz *et al.*, 1998b), while other protein markers were no longer detectable. If the extent of protein degradation is assessed on the basis of

the relative abundance of the other protein pyrolysis products in the fossil elytron, a decay state beyond that reached after 64 weeks in *Manduca* cuticle is suggested, with the onset of significant protein decay reflected in a decrease in relative abundance of protein pyrolysis markers. In common with the pupal cases, the persistence of 2,5-diketopiperazines in the fossil elytron suggests a level of preservation equivalent to less than 2 weeks decayed *Neogonodactylus oerstedii* (Stankiewicz *et al.*, 1998b), reflecting the much lower decay-resistance of crustacean cuticle under marine conditions.

2. 3. 2. 5. 7. Composition of a beetle elytron recovered from Beverley (sample 11)

The pyrolysate (Figure 2. 26 (a)) of this 14th-15th Century beetle elytron from a cess pit in Beverley comprises the characteristic products of chitin and protein. The pyrolysate is dominated by the protein markers indole **(29)** and C_1-indole **(35)**, and the chitin markers 3-acetamidofuran **(25)**, 3-acetamido-5-methylfuran **(30)** and oxazoline structures **(37)**. The distribution and relative abundances of the pyrolysis products is broadly similar to that obtained from modern mealworm beetle cuticle (Stankiewicz *et al.*, 1996; Duncan, 1997) and modern weevil cuticle (Figure 2. 22.(a)), although there are some differences. With the exception of indole **(29)** and C_1-indole **(35)**, the relative abundances of the protein moieties are low. Noticeably, the abundance of C_1-phenol **(18)** is usually high relative to phenol, but in this fossil elytron these compounds are of very similar abundance. This may be attributed to taxonomic variation in cuticle composition, as the fossil elytra are unlikely to represent any of the modern reference taxa. While C_1-phenol is significantly dominant over phenol in the modern mealworm and weevil pyrolysates, the *Manduca sexta* cuticle has similar abundances of the two compounds. However,



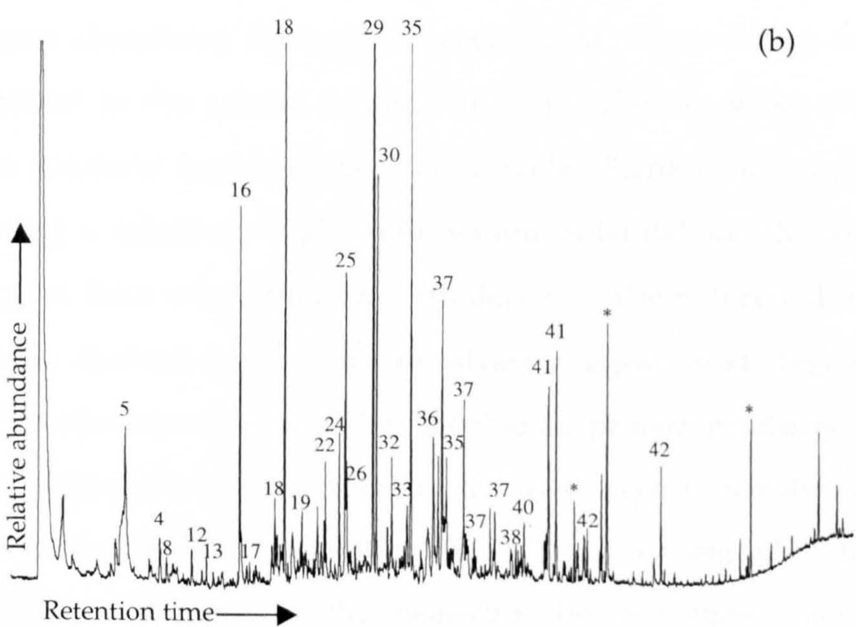


Figure 2. 26. Pyrograms of beetle cuticles., (a) sub-fossil elytron from cess pit at Beverley (Sample 11) and (b) sub-fossil elytron from cess pit at St. Saviourgate (Sample 15).

while these protein moieties are among the most abundant compounds in the pyrolysate of *Manduca* cuticle, they are very minor products in the fossil elytron pyrolysate, suggesting that their source molecules have undergone degradation. Protein moieties such as phenol were generated in increasing relative abundances in the pyrolysates of progressively longer decayed *Manduca* cuticles during the first 32 weeks of laboratory decay, but showed a decrease in relative abundance in the 64 weeks pyrolysate. It is likely that the fossil elytron represents a stage of degradation beyond the 64 weeks decayed *Manduca* cuticle, as protein products such as phenol and C_1-phenol are present in low relative abundances, following decay of their source proteins.

Although the presence of high relative abundances of indole and C_1-indole in the fossil elytron pyrolysate appears to contradict the notion of protein degradation, these protein moieties remained relatively unaltered in relative abundance through 64 weeks of *Manduca* decay, and indole was present in the mantis shrimp cuticle pyrolysates when many other protein products had become undetectable (Stankiewicz *et al.*, 1998b), suggesting a relatively high preservation potential for the amino acid tryptophan, from which they are both derived. The reduced abundance of acetamide derived from chitin pyrolysis suggests that degradation of chitin has also commenced. The fact that all protein products, including 2,5-diketopiperazines, are present in the fossil elytron pyrolysate implies that it has reached only a relatively early stage of degradation, broadly equivalent to the cuticle of the mealworm beetle (*Tenebrio molitor*) after it had been decayed in a natural freshwater setting for 30 weeks (Duncan, 1997); all protein moieties were still detectable in the *Tenebrio* cuticle pyrolysate at this stage. This indicates a much slower rate of decay than for the crustacean *Neogonodactylus oerstedii*, cuticle (Stankiewicz *et al.*, 1998b) which had reached this stage in less than 2 weeks under marine

conditions. This reflects the much slower decay rate of the sclerotised cuticles of insects versus the non-sclerotised, partially mineralised crustacean cuticle, and perhaps also a higher decay rate in marine versus freshwater settings.

2. 3. 2. 5. 8. Composition of a St. Saviourgate beetle elytron (sample 15)

The pyrolysate of this 16th Century St. Saviourgate beetle elytron (Figure 2. 26. (b)) comprises a very similar distribution of compounds to those of the modern weevil (Figure 2. 22. (a)) and mealworm (Stankiewicz *et al.*, 1996; Duncan, 1997) beetles. The fossil beetle elytron pyrogram is dominated by the protein markers phenol **(16)**, indole **(29)** and C_1-indole **(35)**, and the chitin products C_2-pyridine **(9)**, 3-acetamidofuran **(25)**, 3-acetamido-5-methylfuran **(30)** and oxazoline structures **(37)**. C_2-phenol **(22)** and 2,5-diketopiperazine derivatives **(41)**, derived from proteins, are also relatively abundant. Despite retaining the same range of compounds as the modern reference specimens, there are some minor differences in their relative abundances. In the fossil elytron, phenol is present in higher abundance relative to the major chitin marker acetamide, which has reduced in relative abundance compared to the modern beetle pyrolysates. The taxonomic identity of the cess pit elytron is unknown, so that the observed differences in composition may be partly due to taxonomic variation. Although phenol is a relatively insignificant product in both the weevil and mealworm cuticle pyrolysates, it is one of the major products of Manduca *sexta* cuticle pyrolysis, so that its observed relative abundance in the cess pit elytron may typify the original elytron composition. This is supported by the fact that, in common with all of the modern insect cuticle pyrolysates used for comparison, C_1-phenol has a higher relative abundance than phenol in the cess pit elytron, perhaps indicating that negligible protein

degradation has taken place. The abundance of phenol in the *Manduca* pyrolysates increased to exceed that of C_1-phenol as early as 4 weeks of decay, and continued to rise beyond 32 weeks, only decreasing again by 64 weeks. The high relative abundance of other protein moieties, such as indole and C_1-indole, suggest that the fossil elytron has undergone only negligible decay, perhaps equivalent to the first 4 weeks of decay of *Manduca sexta* cuticle in the laboratory.

Some degradation of the cess pit beetle elytron is suggested by the fact that acetamide/pyrrole is present in much lower abundance than in any of the modern cuticle pyrolysates. On the basis of the reduction in the relative size of this peak, this beetle elytron has reached a degradation stage equivalent to mealworm cuticle decayed for between 2 and 30 weeks in a freshwater pond (Duncan, 1997).

Despite a general persistence of chitin products over protein moieties during degradation of the mantis shrimp *Neogonodactylus oerstedii* (Stankiewicz *et al.*, 1998b), a pronounced reduction in the acetamide/pyrrole peak was observed. This is possibly partially due to chitin degradation and partly to degradation of the other compounds that co-elute with acetamide over its prolonged elution period. A combined reduction in the yield of these markers from pyrolysis, due to decay of their source molecules, results in an apparent reduction in the overall peak area. As with the other cess pit fossils discussed above, the persistence of all protein products, including 2,5-diketopiperazines, indicates that this elytron represents a very early stage of degradation, equivalent to less than 2 weeks of decay in *Neogonodactylus oerstedii* (Stankiewicz *et al.*, 1998b).

2. 3. 3. Mineralogy and elemental composition of the mineralised faecal concretions

EDX (Energy Dispersive X-ray) analysis reveals that the mineralised fossils and concretions from the archaeological cess pits and stable floor are composed of calcium phosphate (Figures 2. 7., 2. 8. & 2. 21).

There is significant variation in the elemental compositions of mineralised faecal concretions from the cess pits and stable floor (concretion 84), although all have fairly similar, high concentrations of Ca and P consistent with a calcium phosphate mineralogy (see Table 2. 10. and Figures 2. 27. to 2. 34.). Al is present in fairly similar concentrations in all of the concretions except concretion 17, which has a higher concentration than the others. The concentration of Fe in the concretions is quite varied, but that in concretion 105 is an order of magnitude higher than in the others. Relatively similar concentrations of Mg are present in the concretions, with the exception of concretion 105 which has a higher concentration, and concretion 11 in which a relatively low Mg concentration was measured. K content varies, but only within a narrow range of concentrations. In the concretions, concentrations of Mn are highest in concretion 105 but the two stable concretions (84 and Twig 84) have Mn concentrations which exceed those of all of the concretions. Similarly, higher Na concentrations were recorded in the stable concretions than in the concretions, which were fairly uniform in Na content. Among the cess pit concretions, sample 105 was most distinct from the others, with higher concentrations of Fe, Mg, K and Mn.

To investigate how phosphatisation in terrestrial archaeological deposits compares with phosphatisation in the marine settings in which it is more fully understood, the elemental compositions of the cess pit

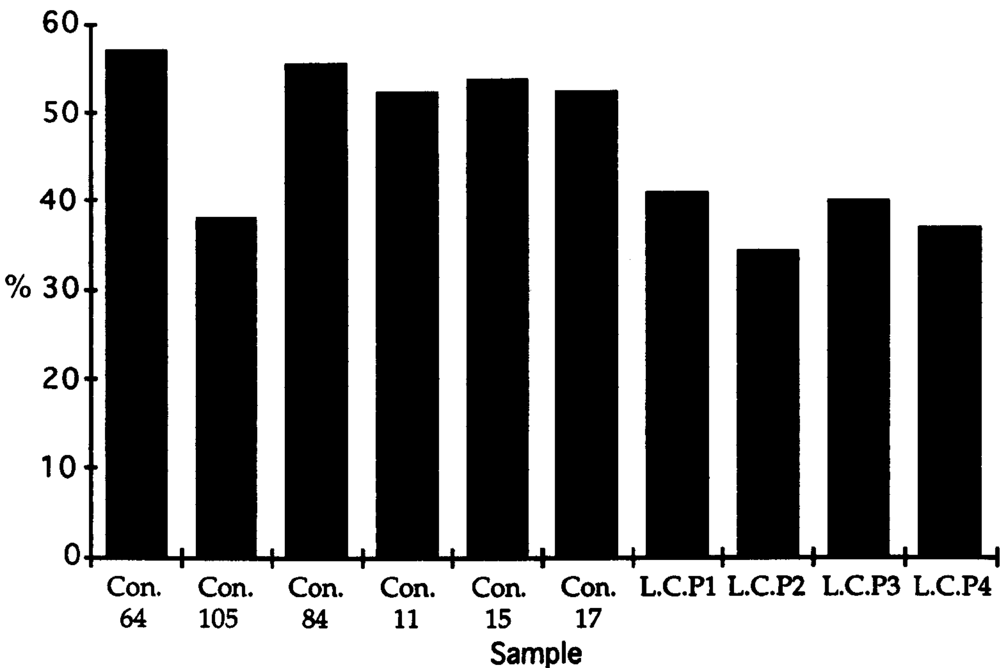


Figure 2. 27. % contribution of Ca to mineralised faecal concretions from ancient cess pits in and around York, and concretions from the London Clay. Con. n. = concretion recovered from sample n. L.C.P.1-4 refer to elemental compositions at different positions in a London Clay concretion analysed by Allison (1998b), where L.C.P.1 represents the core and L.C.P.4 the outer rim.

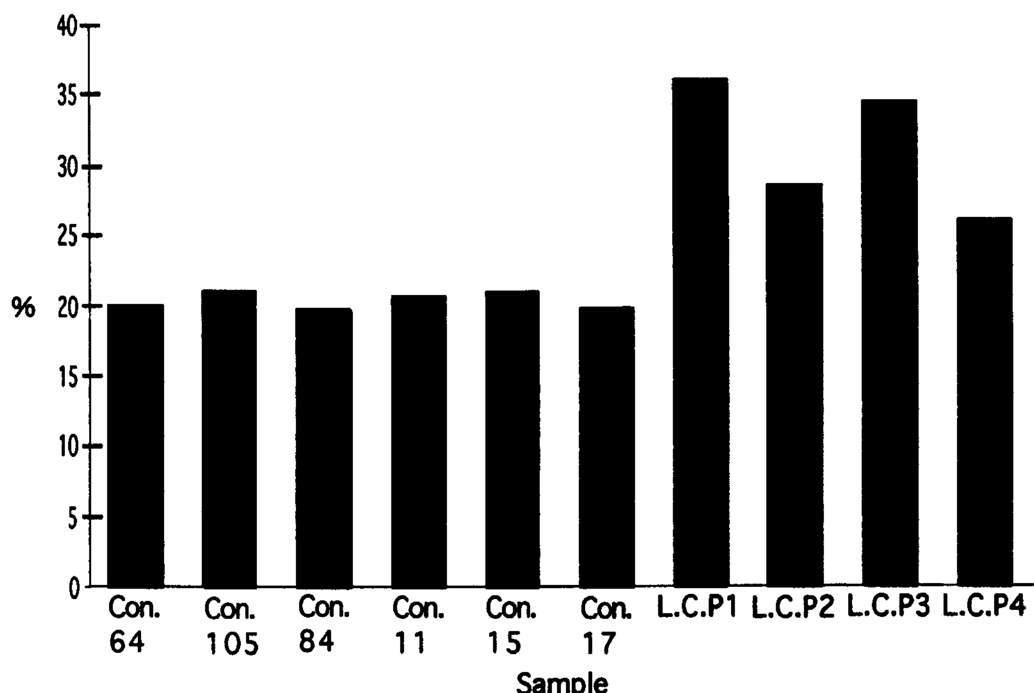


Figure 2. 28. % contribution of P to mineralised faecal concretions from ancient cess pits in and around York, and concretions from the London Clay. Con. n. = concretion recovered from sample n. L.C.P.1-4 refer to elemental compositions at different positions in a London Clay concretion analysed by Allison (1988b), where L.C.P1 represents the core and L.C.P.4 the outer rim.

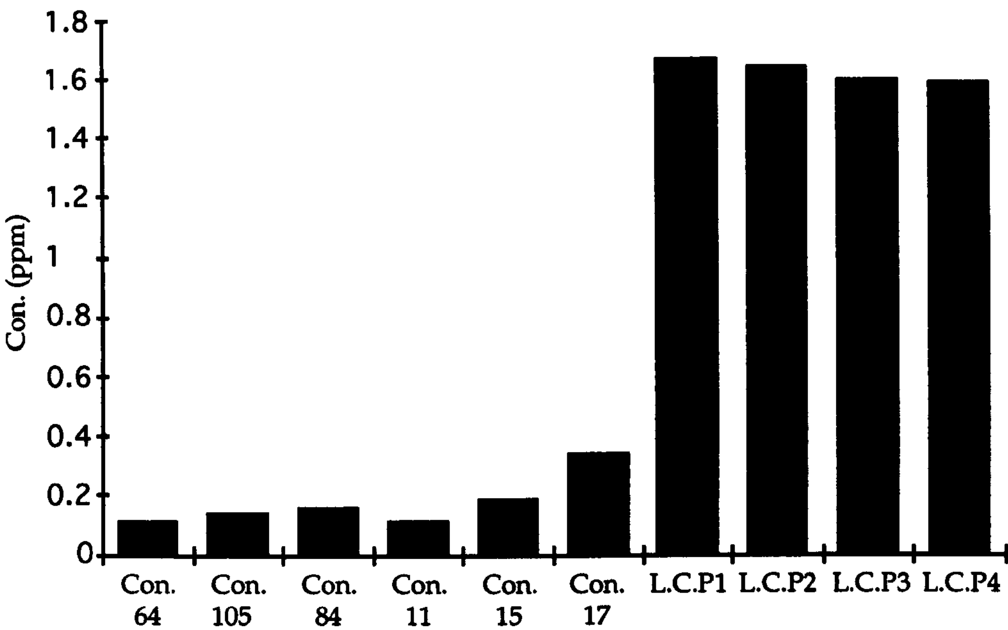


Figure 2. 29. Concentrations of Al in cess pit faecal concretions and concretions from the London Clay. Con. n. = concretion recovered from sample n. L.C.P1-4 refer to elemental concentrations at different positions in a London Clay phosphatic concretion analysed by Allison (1988b), where L.C.P1 represents the core of the concretion and L.C.P4 the outer rim.

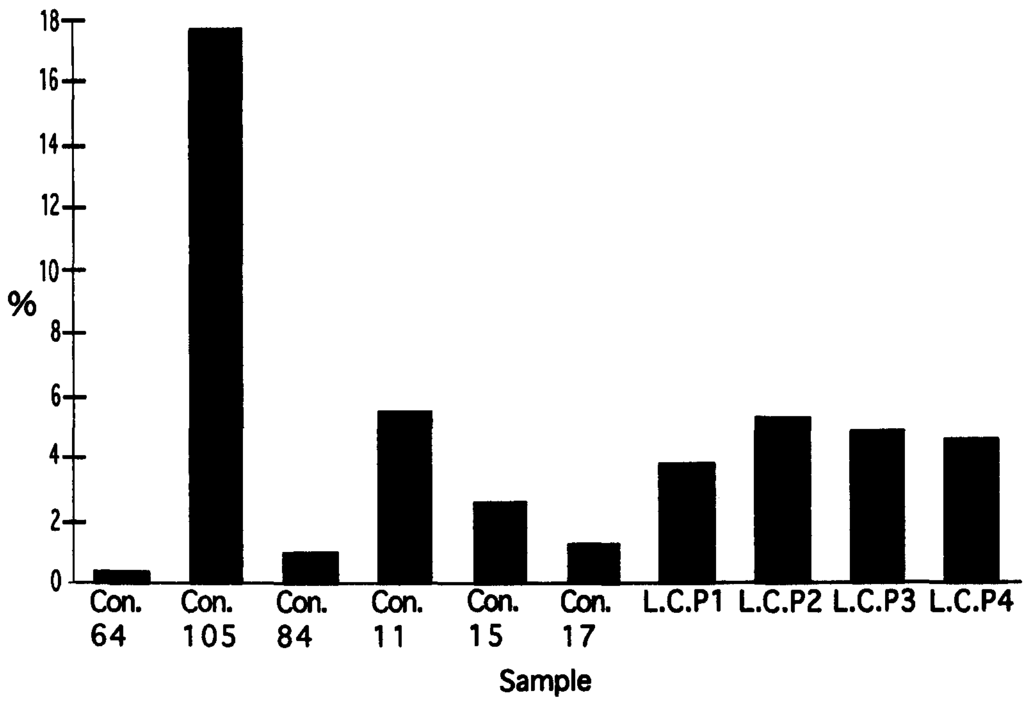


Figure 2. 30. % contribution of Fe to mineralised faecal concretions from ancient cess pits in and around York, and concretions from the London Clay. Con. n. = concretion recovered from sample n. L.C.P.1-4 refer to elemental compositions at different positions in a London Clay concretion analysed by Allison (1988b), where L.C.P1 represents the core and L.C.P.4 the outer rim.

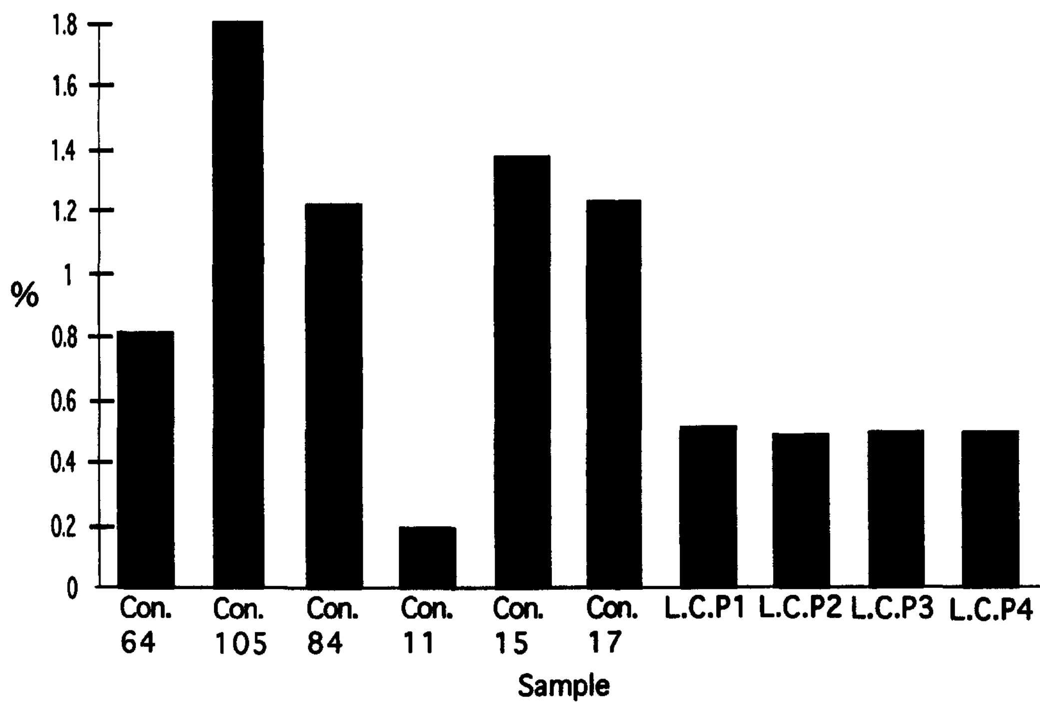


Figure 2. 31. % contribution of Mg to mineralised faecal concretions from ancient cess pits in and around York, and concretions from the London Clay. Con. n. = concretion recovered from sample n. L.C.P.1-4 refer to elemental compositions at different positions in a London Clay concretion analysed by Allison (1988b), where L.C.P.1 represents the core and L.C.P.4 the outer rim.

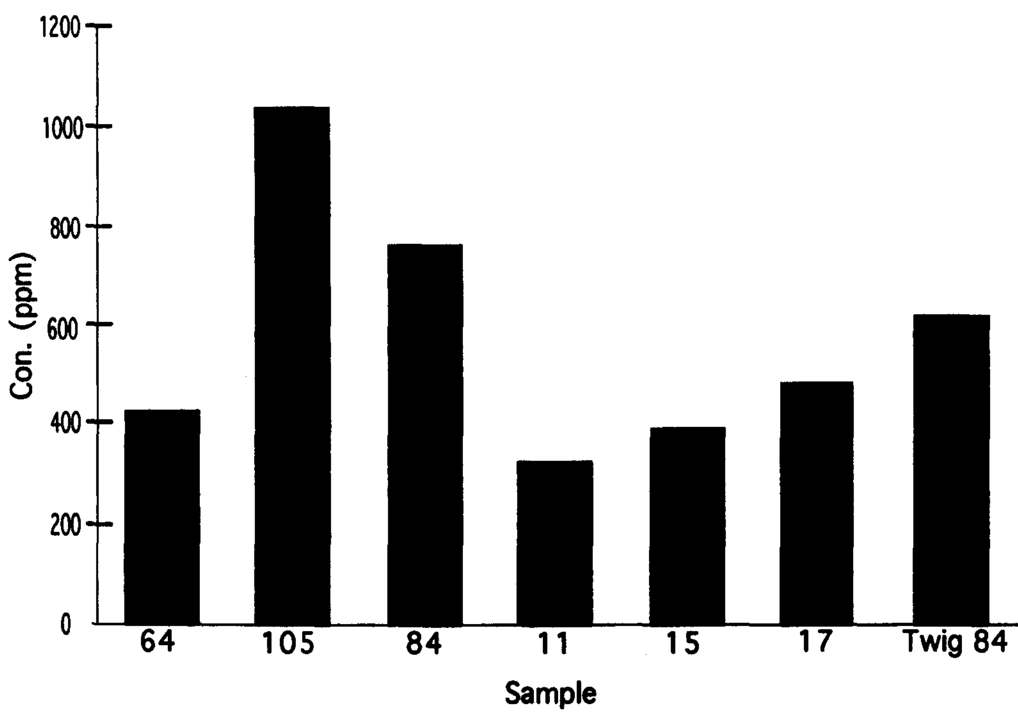


Figure 2. 32. Concentration of K in mineralised faecal concretions from ancient cess pits in and around York.

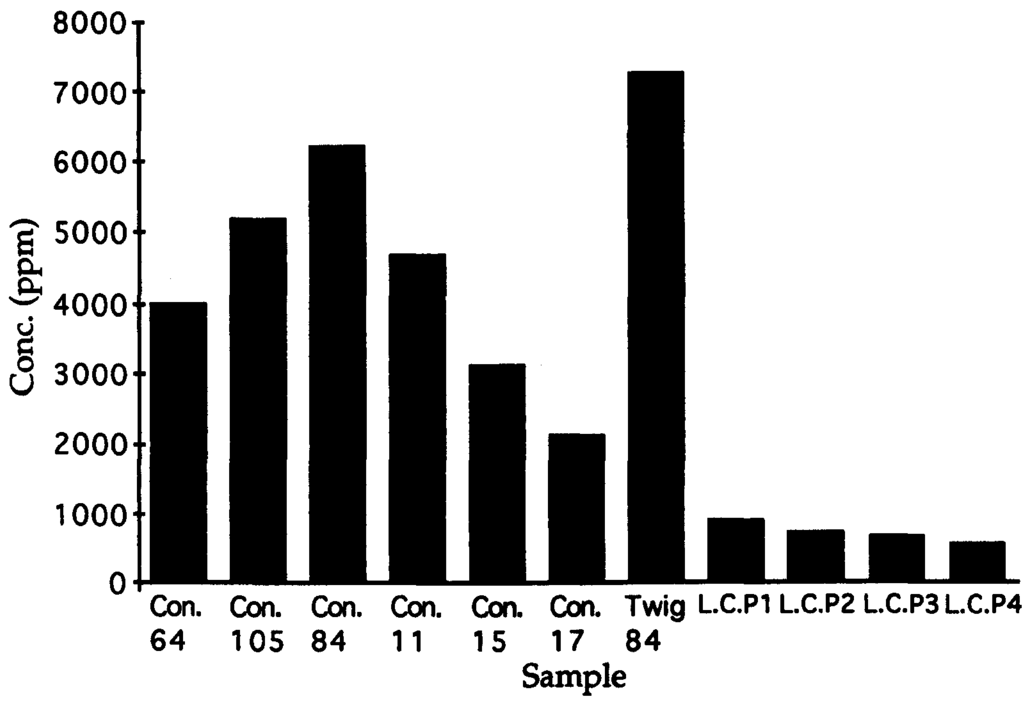


Figure 2. 33. Concentrations of Mn in mineralised faecal concretions from ancient cess pits, concretions and a twig from an ancient stable floor in and around York, and concretions from the London Clay. Con. n. = concretion recovered from sample n. L.C.P1-4 refer to elemental concretions at different positions in a London Clay concretion analysed by Allison (1988b), where L.C.P1 represents the core and L.C.P4 the outer rim.

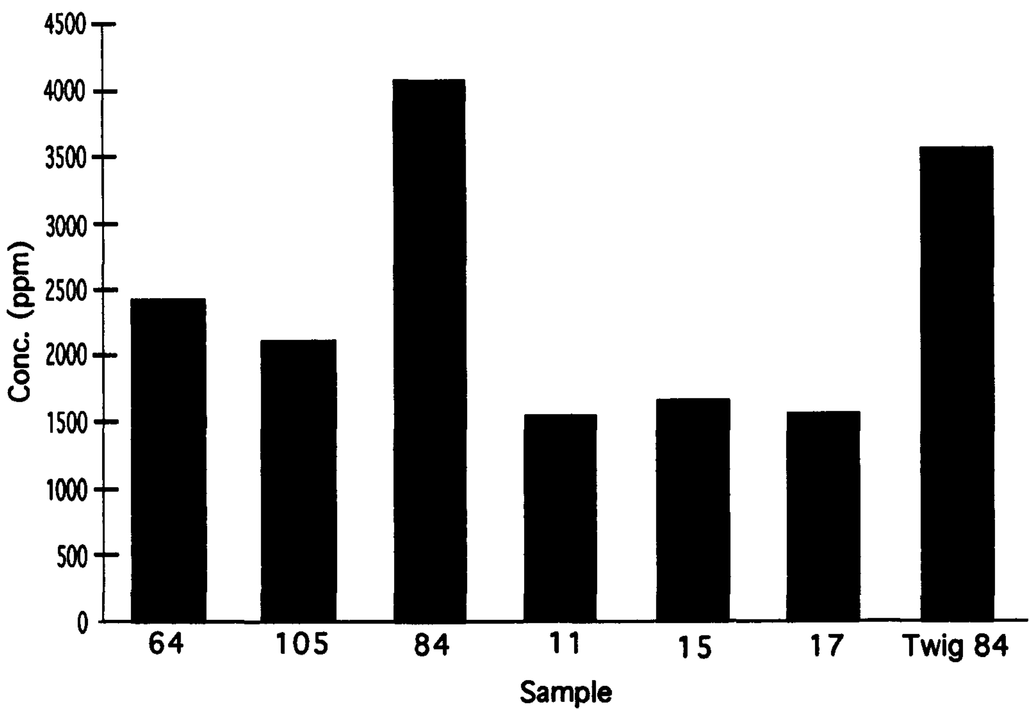


Figure 2. 34. Concentration of Na in mineralised faecal concretions from ancient cess pits in and around York, and in a mineralised twig recovered from an ancient stable floor (Allison, 1988b, did not measure Na in London Clay concretions).

phosphatised concretions were compared with those of phosphatised concretions from the Eocene London Clay (Allison, 1988b. Graphs 3. 5. a - e). Although the concentration of Si is included in the data for the London Clay concretions, it was not possible to measure this element in the cess pit concretions.

Table 2. 10. Elemental composition of mineralised faecal concretions from the York archaeological cess pit concretions (ICP-AES). Data are concentrations in parts per million.

Element	P	Al	Fe	Mn	Ca	Na	K
64	87000	468.5	1955	3985	248500	2415	425
105	106500	715	91000	5200	248500	2415	425
84	82000	670	3915	6200	232500	4060	755
11	87000	470	23350	4660	222000	1550	323
15	83500	765	10100	3095	215500	1650	387.5
17	77500	1355	4730	2090	208000	1555	478

Hence, to make the cess pit concretion data comparable with the London Clay data, the percentage contribution from the other major elements was calculated by assuming that the measured elements comprised 75. 5 % (the mean total contribution of these elements to the London Clay concretions when Si was excluded).

The percentage contribution of Al to the cess pit concretions is much lower than to the London Clay concretions, and the percentage of P is also lower. Concentrations of Mn in the cess pit concretions, and percentages of Ca and Mg, are typically higher than in the London Clay concretions, although concretion 11 has a lower Mg content than the London Clay concretions. Concretion 11 has iron levels comparable to the London Clay concretions, while concretions 64, 84 and 15 have less iron in them, and concretion 105 has an iron content far exceeding all of the other concretions. The number of concretions analysed is too low to allow

rigorous statistical confirmation of the compositional trends observed (with only five cess pit concretion concretions and four London Clay concretions for each element). The results of Student's t-tests indicate that Fe is the only element which does not differ significantly in concentration between the cess pit and London Clay concretions. The concentration of Al and P is significantly less in the cess pit concretions ($p < 0.001$ and $p < 0.01$ respectively). Conversely, the concentration of Ca, Mn and Mg is significantly more in the cess pit concretions ($p < 0.01$, 0.01 and 0. 05 respectively).

2. 3. 4. Sediments

2. 3. 4. 1. Grain size distributions

The results generated by the MASTERSIZER used to obtain the size distribution for sediment grains below 212 μm are in the form of percentiles (see Appendix 3), so that the exact percentage of sediment in each grain size bracket could not be accurately established. Instead, values covering the possible range of percentages in each grain size class (sand, silt and clay) were plotted on a ternary diagram (Figure 2. 35.; after Rowell, 1994) to obtain the textural class for each sample. All samples fell within the sandy loam class with the exception of Sample 11 which is a slightly finer grained sandy silt loam.

2. 3. 4. 2. Total organic carbon, hydrogen and nitrogen

The results are summarised in Figure 2. 36. There is considerable variation in the percentages of Total Organic C, H and N in the different soil samples, with no apparent relationship to sample age, although the highest percentages of the three elements remain in one of the two youngest samples.

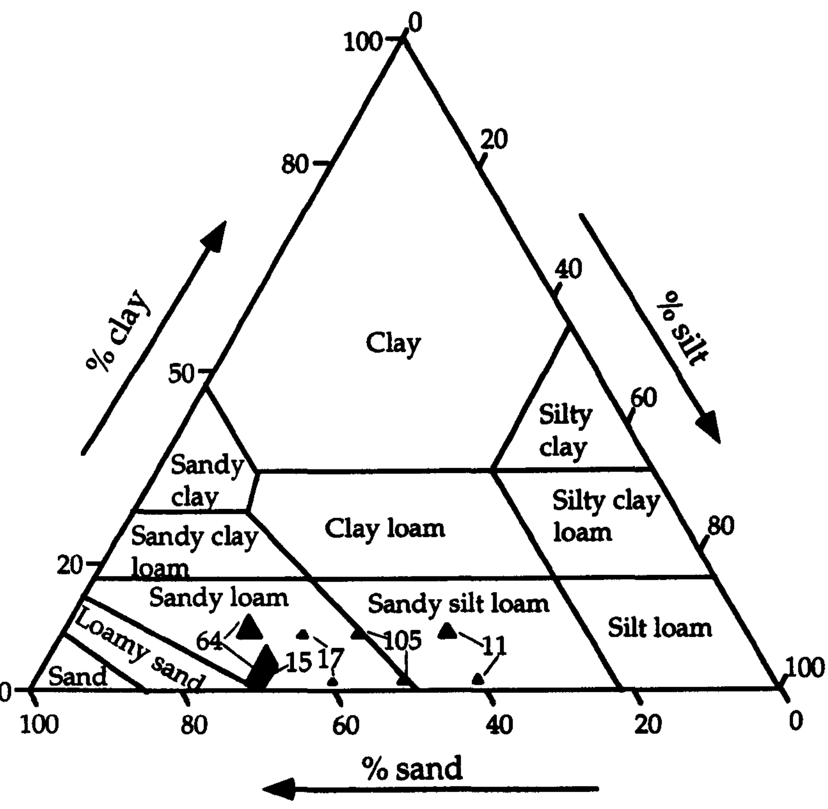


Figure 2. 35. Ternary plot showing the ranges of possible grain sizes of the sediment samples studied from ancient cess pits in and around York. Plot drawn according to the UK system for soil textural classification (after Rowell, 1994).

2. 3. 4. 3. **pH and elemental composition of the soil solutions**

The pH of all of the soil solutions is mildly acidic pH, within a narrow band between pH 4. 95 and pH 5. 57 (Table 2. 11.). The results of ICP-AES analysis of Na, Mg, Al, P, K, Ca, Mn and Fe in the soil solutions are summarised in Figure 2. 37. - 2.44., along with mean concentrations of the elements in river and ocean water (Riley & Chester, 1971), and in soil solutions extracted using immiscible liquid displacement centrifugation from woodland and grassland sites in Oxfordshire (Campbell *et al*, 1989; concentrations converted from mmol m^{-3} to p. p. m. using conversion factors in Edmunds, 1986).

Table 2. 11. pH of the archaeological cess pit pore waters.

Sample	pH
11	5. 15
64	5. 57
17	4. 95
105	5. 25
15	5. 30

Elemental concentrations are fairly uniform for all of the soil solutions with the notable exception of Sample 11. The soil solution from this sample has much higher concentrations of Fe, Mn and P than that from the other soil samples, as well as more Al, and less Mg and K. Sample 105 has a significantly higher K concentration than the other sample solutions.

Concentrations of Ca and P are generally higher in the cess pit soil solutions than in fresh, marine and soil pore waters, although the P content of Sample 105 is within the range of woodland and grassland soil solutions. Concentrations of Fe and Al are greater in the cess pit samples than in marine water, and are similar to grassland clay soil solutions, but are in general less than fresh water, woodland and grassland sandy soil

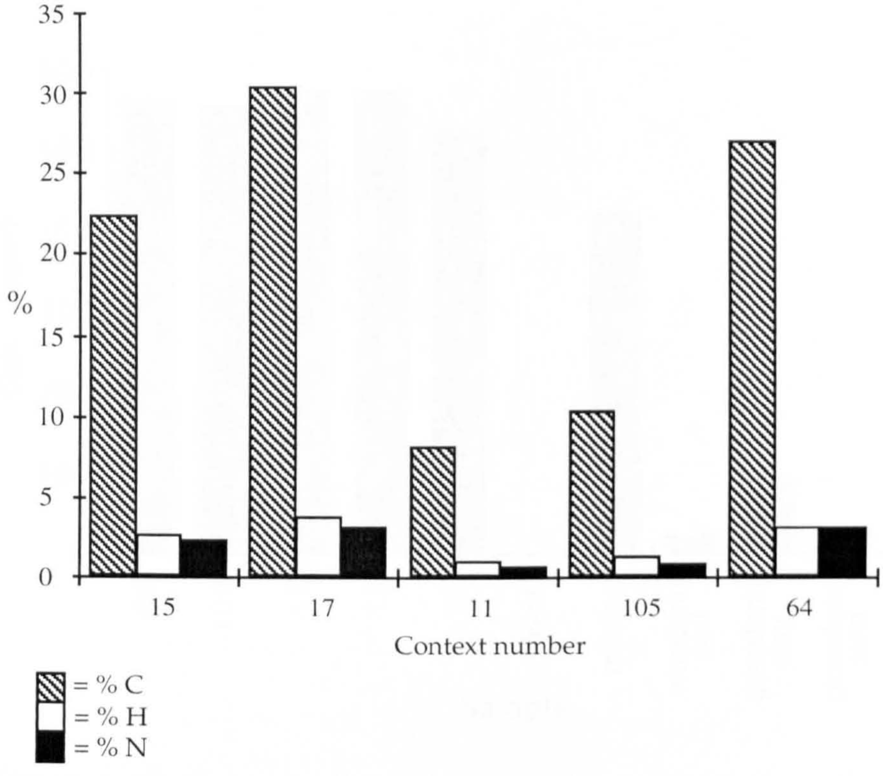


Figure 2. 36. Total organic C, H and N in soils from the York archaeological contexts studied.

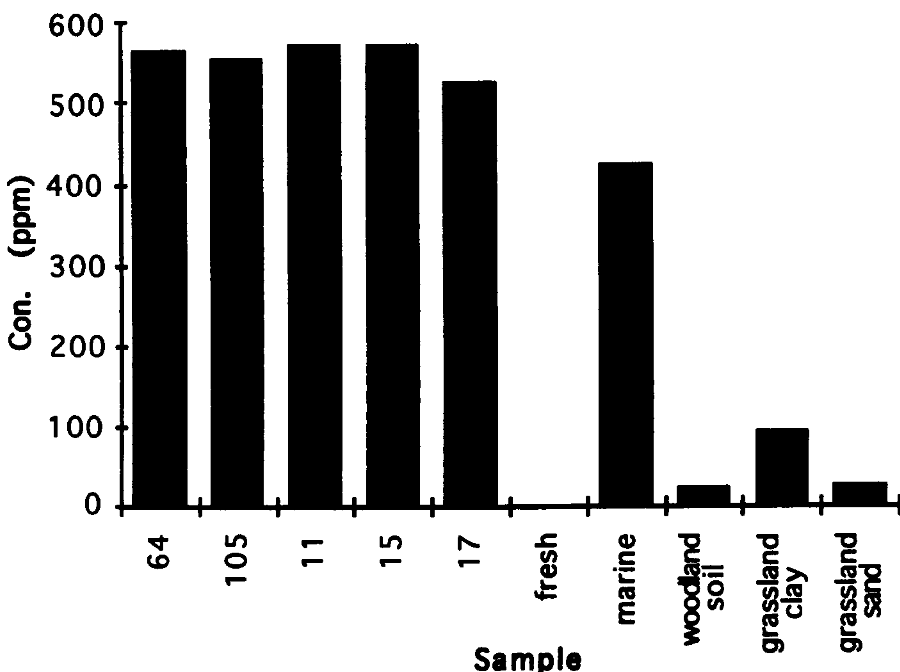


Figure 2. 37. Concentrations of Ca in soil pore waters from the York cess pit contexts studied, from fresh and marine waters, and from pore waters of woodland, grassland clay and grassland sandy soils.

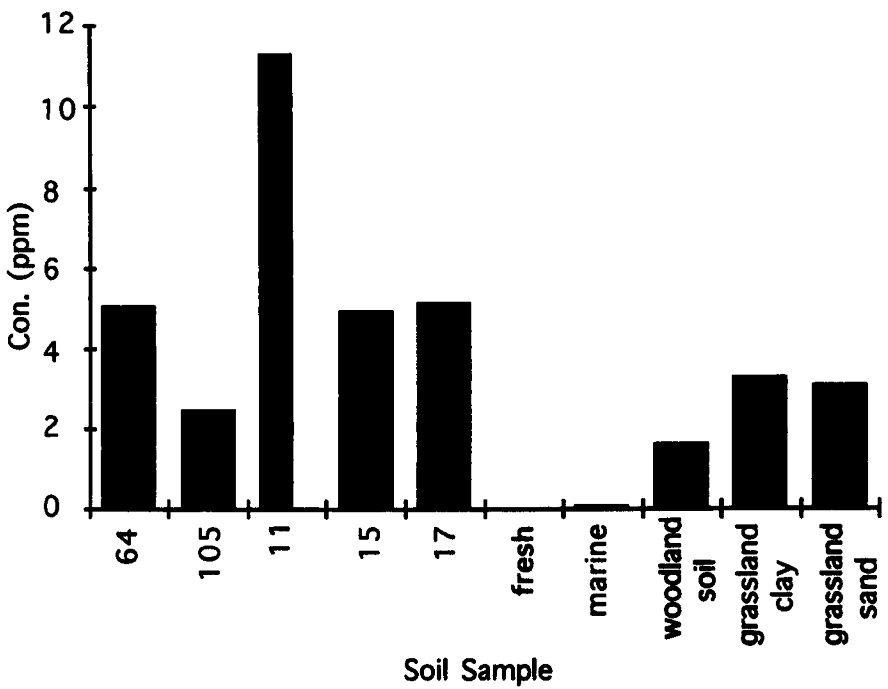


Figure 2. 38. Concentrations of P in soil sample pore waters from each of the York cess pit contexts studied, and from modern fresh and marinewaters, and pore waters from woodland, grassland clay and grassland sandy soils.

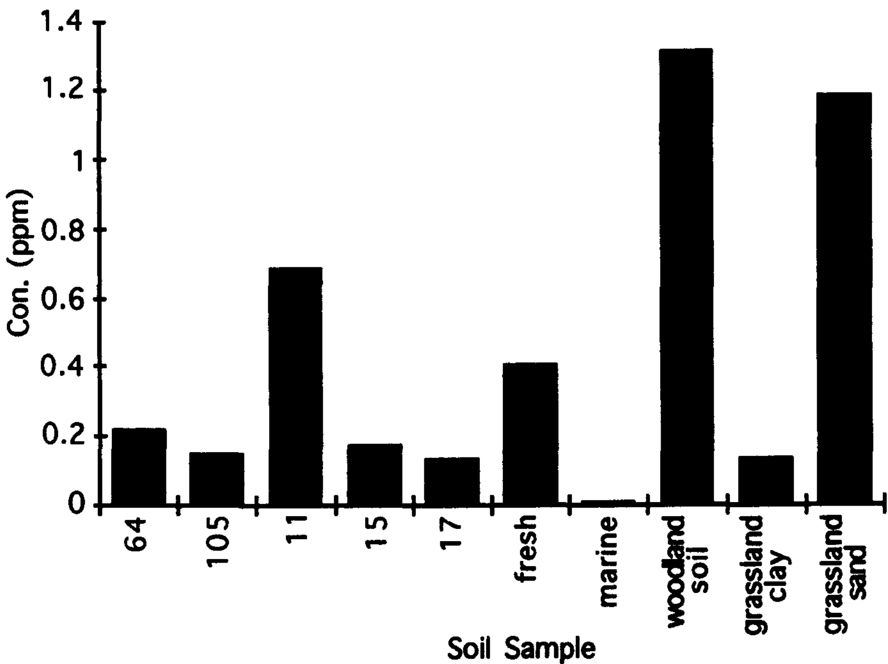


Figure 2. 39. Concentrations of Al in soil pore waters from the York cess pit contexts studied, from fresh and marine waters, and from pore waters of woodland, grassland clay and grassland sandy soils.

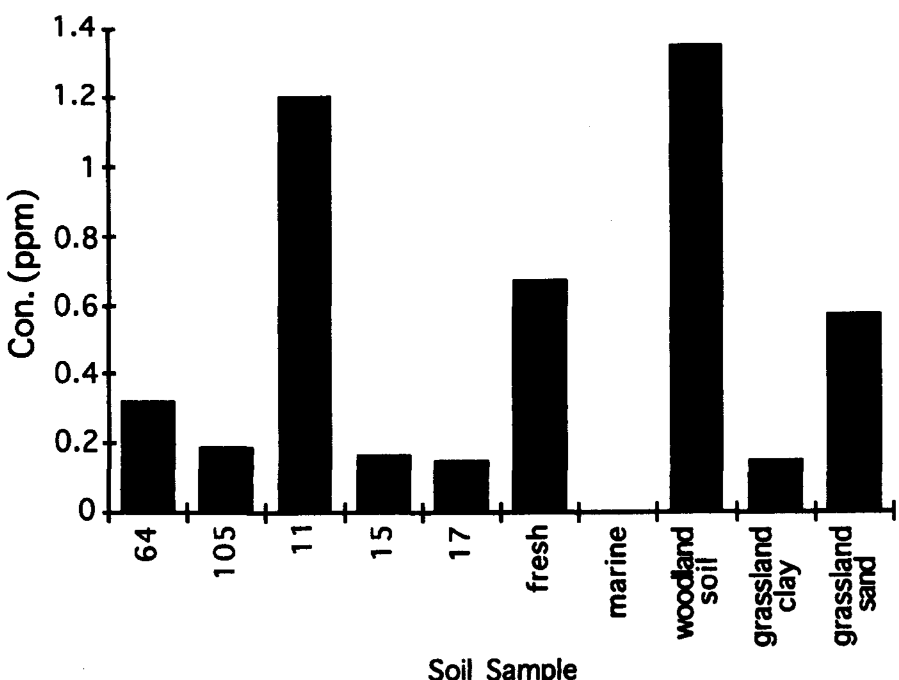


Figure 2. 40. Concentrations of Fe in soil samples from the York cess pit contexts studied, and modern fresh and marine waters, and pore waters from woodland, grassland clay and grassland sandy soils.

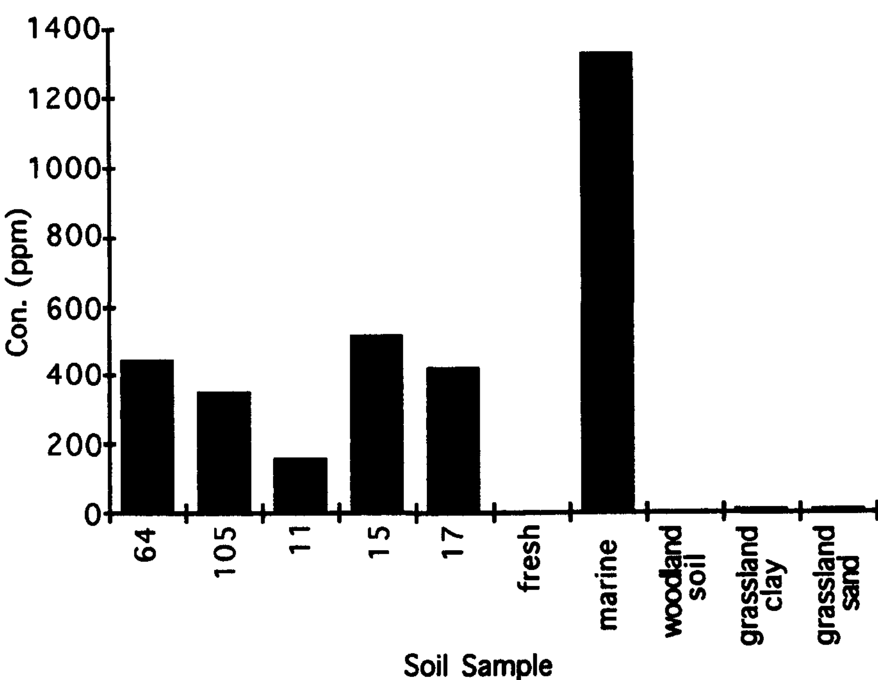


Figure 2. 41. Concentrations of Mg in soil sample pore waters from the York cess pit contexts studied, andfrom modern fresh and marine waters, and pore waters from woodland, grassland clay and grassland sandy soils.

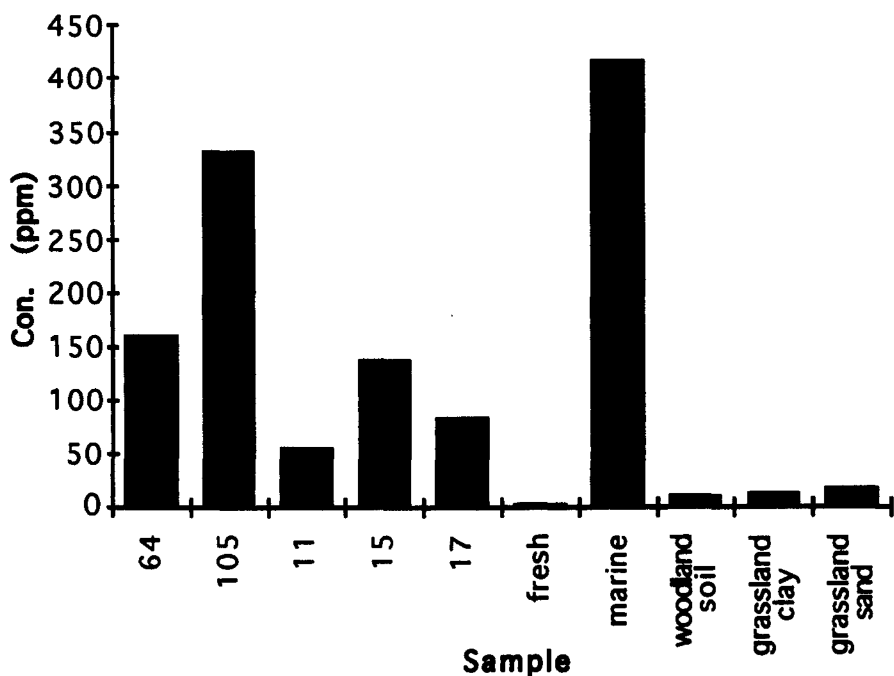


Figure 2. 42. Concentration of K in soil sample pore waters from the York cess pit contexts studied, and from modern fresh and marine waters, and pore waters from woodland, grassland clay and grassland sandy soils.

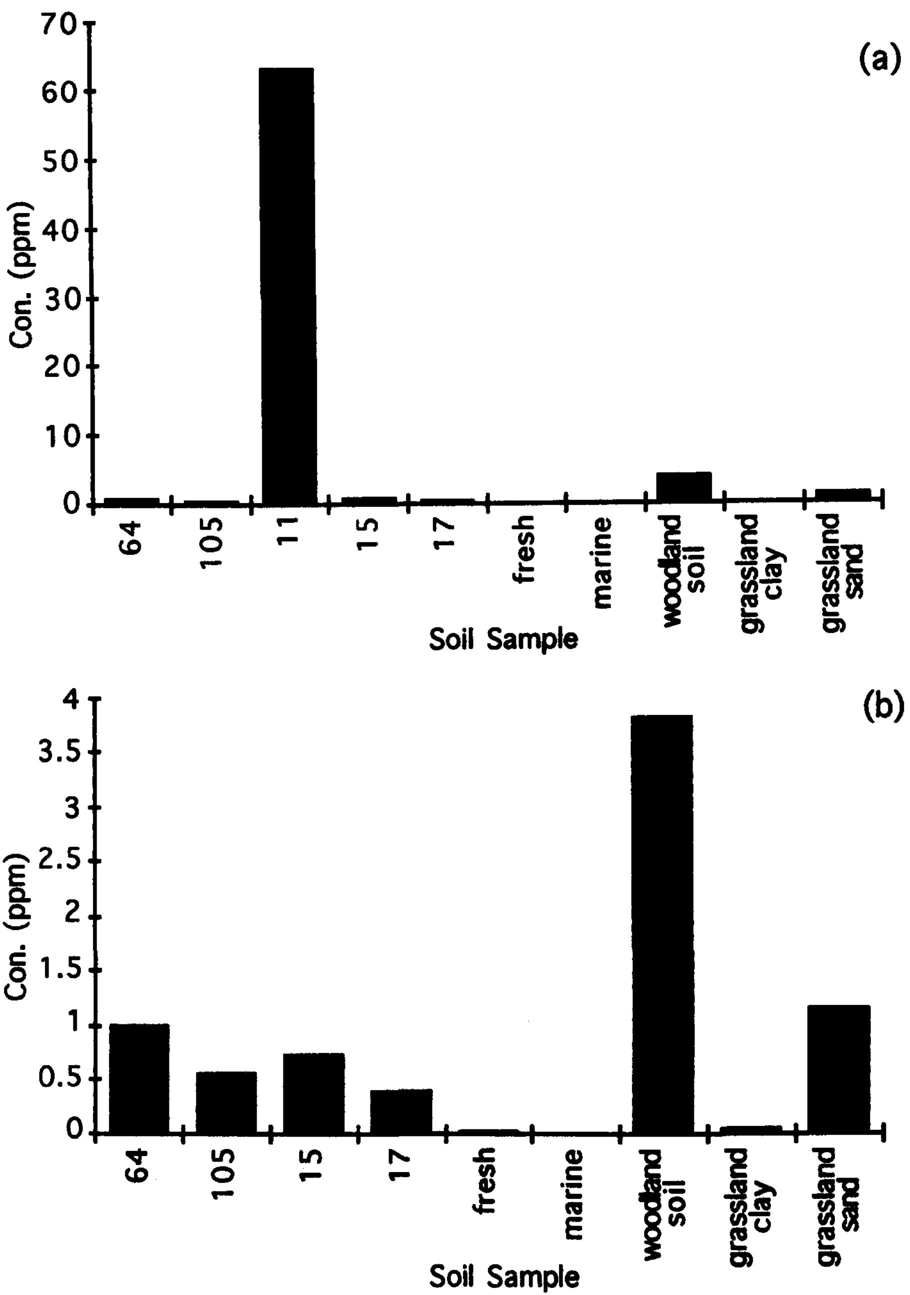


Figure 2. 43. Concentrations of Mn in (a) soil sample pore waters from the York cess pits studied, and from modern fresh and marine waters, and pore waters from woodland, grassland clay and grassland sandy soils.
(b) as (a) but excluding sample 11, whose high Mn con. obscures that of the other soil pore water samples.

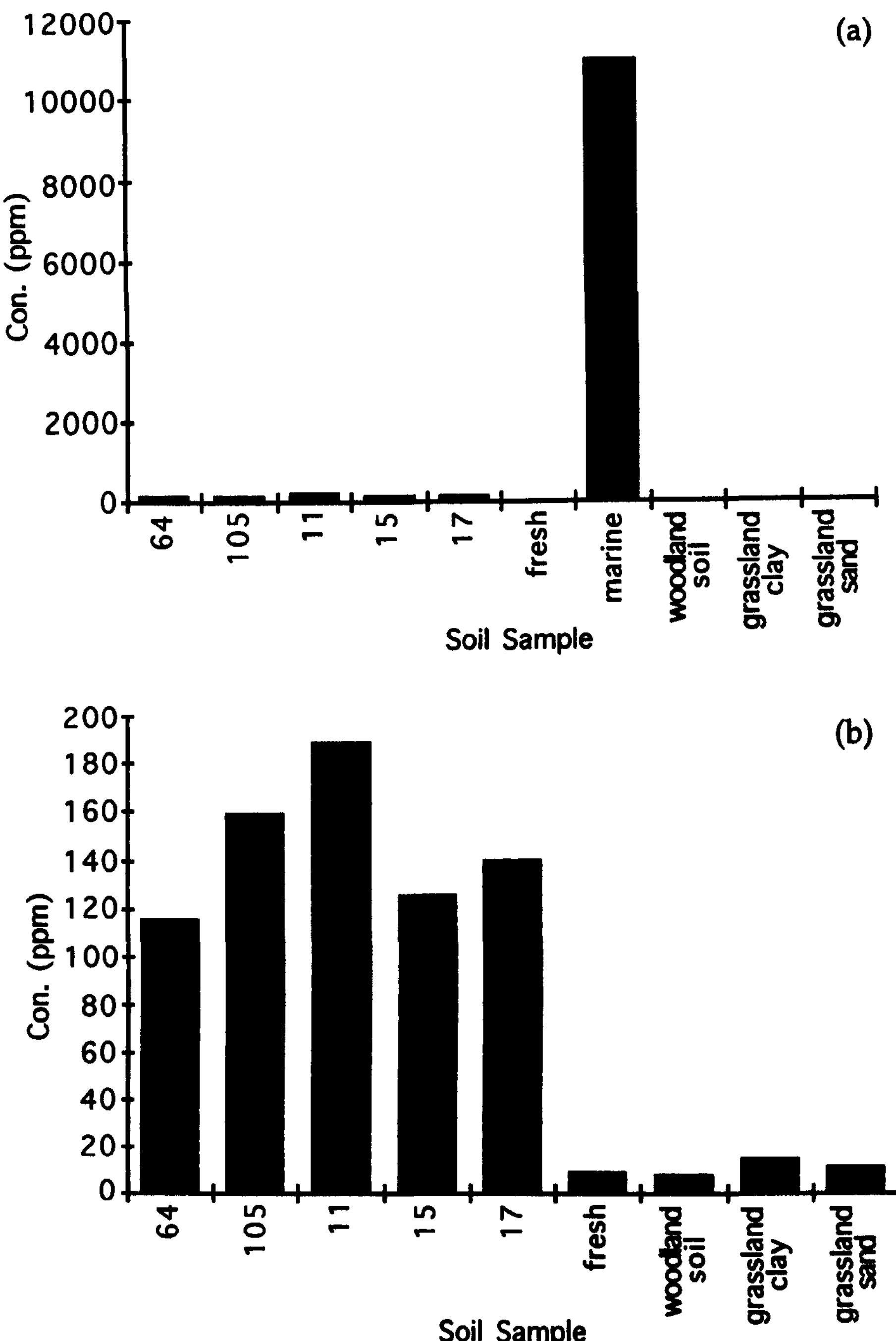


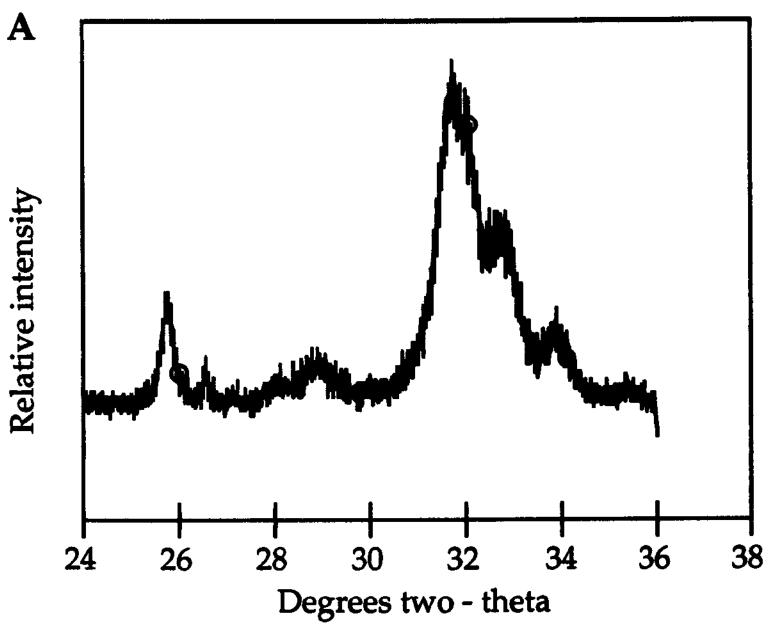
Figure 2. 44. Concentrations of Na in (a) soil pore waters from the York cess pit contexts studied, fresh and marine waters, and pore waters from woodland, grassland clay and grassland sandy soils. (b) as (a), excluding marine waters.

levels. Al and Fe levels in Sample 11 are higher than in fresh water; the concentration of Fe in this sample is exceeded only by that in the woodland soil solution, and that of Al, in both woodland soil and grassland sandy soil solutions. Na, Mg and K all show a similar pattern; concentrations are much higher in the cess pit samples than in fresh and soil pore waters, but significantly lower than in sea water. Concentrations of Mn in the cess pit soil solutions are greater than those in fresh, marine and grassland clay pore waters, similar to that in grassland sandy soil pore waters but, on average, less than that in woodland soil pore waters. The one exception to this is Sample 11: the Mn concentration in this sample is an order of magnitude higher than woodland soil pore waters.

2. 3. 5. Bones

2. 3. 5. 1. Crystallinity of the cess pit, Barton-on-Humber and fresh bones

The extent of alteration of bones and bone fragments recovered from the ancient cess pits was assessed by measuring changes in the crystallinity of the hydroxyapatite which makes up the mineral fraction, using X-ray Diffraction. Figure 2. 45. shows the X-ray diffractograms for a bone specimen from one of the cess pit samples studied and for a Barton-on-Humber bone. The X-ray diffractogram for fresh bone (Figure 2. 1.) is characterised by a very diffuse pattern, in which the three main apatite peaks are difficult to distinguish, and very similar diffractograms were obtained for the cess pit bones. Thus Crystallinity Indexes which consider proportions of all three apatite peaks could not be obtained. The Crystallinity Index used was FWHM (Full Width at Half Maximum height), which is based on just the height of the main apatite peak and an estimation of its width. The Barton-on-Humber bones yielded very different X-ray diffraction patterns, in which the three apatite peaks are sharp and clearly distinguishable. Figure 2.46. shows that the Crystallinity



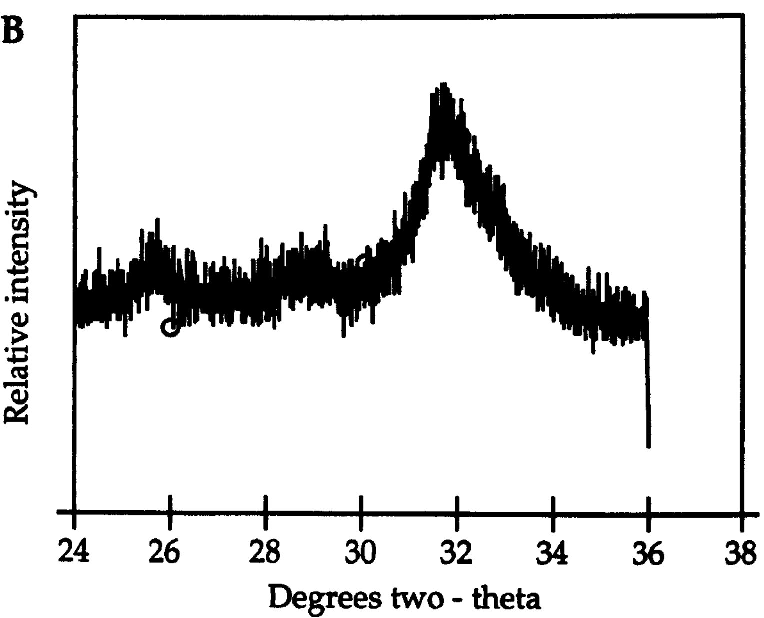


Figure 2. 45. XRD patterns of bones: A. Uncoffined human rib from the 18th-19th Century burial phase of St. Peter's churchyard, Barton-on-Humber. B. Lamb bone from a 4th Century cess pit at St. Saviourgate , York.

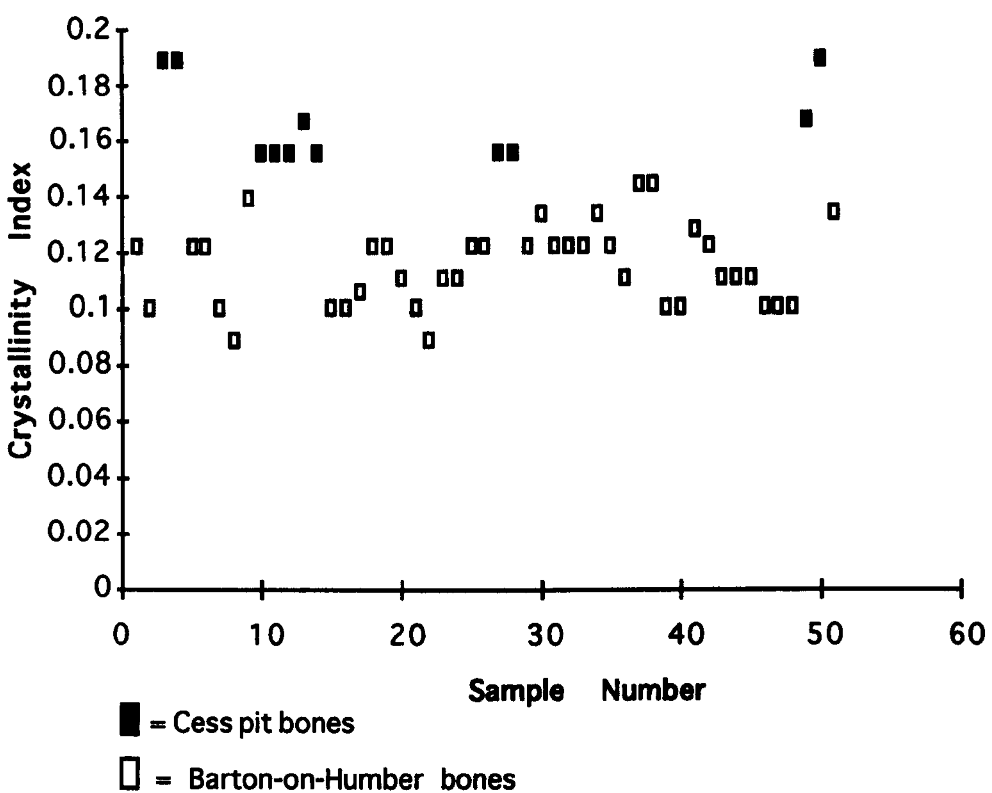


Figure 2. 46. Plot showing the crystallinity indexes calculated from XRD data for the bones studied from ancient cess pits in and around York and a graveyard at Barton-on-Humber.

Index (C. I.) for all of the bones analysed in this study defines two very clear groups. The C. I. of the Barton-on-Humber bones is consistently lower than that of the cess pit bones, indicating that the hydroxyapatite has undergone much more alteration. A Student's t-test confirmed that the difference in the C. I. s of the two groups was very highly significant ($p < 0.001$).

2. 4. Discussion

2. 4. 1. Mineralisation in ancient cess pits

The two major issues which palaeontologists address when investigating fossilisation processes are the conditions under which they occur and the timescale over which they operate. These questions were reiterated in relation to mineralisation in archaeological deposits by Carruthers, in her discussion of phosphatised plant remains from the Bronze Age midden at Potterne (Carruthers, 2000). Carruthers considered that the most important aims for understanding the phosphatisation process in these deposits were establishing the degree of anoxia and extent of waterlogging. The structural and compositional information gained from the mineralised fossils and Samples recovered from the York ancient cess pits go some way towards elucidating the phosphatisation process and its associated conditions in terrestrial settings. This, in turn, may increase our understanding of this mode of fossilisation in the marine deposits with which it is more traditionally associated.

2. 4. 1. 1. The process of phosphatisation

The diagenetic replacement of non-mineralised tissues by authigenic minerals is intimately associated with decay processes, which govern the pH, degree of anoxicity and ionic concentrations of the sediment pore waters in the vicinity of organic matter (Allison, 1990). Where oxygen is

freely available, organic matter is degraded by aerobic microbial respiration but once oxygen supplies have been depleted, alternative electron acceptors must be employed in various anaerobic decay reactions. In an ideal setting, these anaerobic decay pathways are layered in the sediment, with those associated with the greatest free-energy yield at the top of the pile. Nitrate reduction, manganese reduction, iron reduction and sulphate reduction are the main processes, in order of decreasing free-energy yield and increasing sediment depth. In reality, the pathways are not necessarily separated spatially, but the respiratory substrate with the greatest free-energy yield is depleted before the next most productive is employed. The ions produced by these reactions may combine with other pore water ions to form authigenic minerals, the most important being the bicarbonate ion, a common by-product of the reduction pathways. The particular mineral which forms depends upon its stability in the prevailing pore water conditions.

The level of detail preserved in the phosphatised cess pit seeds and invertebrates is not surprising, as calcium phosphate is the mineral most commonly associated with high fidelity soft tissue preservation. Experimental work has shown how phosphatisation is associated with microbial decay processes in marine settings (Briggs & Kear, 1994a). Under normal marine conditions, the high concentration of bicarbonate ions generated by organic decay favours calcium carbonate precipitation, and phosphatisation is inhibited. However, where diffusion is restricted, the concentration of phosphate ions may exceed that of bicarbonate ions, allowing calcium phosphate to precipitate. The relationship between calcium phosphate and calcium carbonate is dynamic and closely linked to decay-induced changes in pH, at least in marine settings (Briggs & Wilby, 1996). Apatite is stable over a wider range of pH than calcium carbonate, and precipitates in the acidic environment created when by-

products of decay such as fatty acids are allowed to accumulate under closed conditions. In these circumstances, calcium carbonate remains in solution but it may precipitate when the pH rises in later stages of decay. Although authigenic calcium carbonate is generally absent from the cess pits, it was observed in one of the Coppergate crab apple pips, where calcium carbonate needle rosettes have overgrown phosphatised cotyledon tissue. The co-occurrence of these two minerals has previously been reported in both fossil (Briggs & Wilby, 1996) and experimentally decayed marine arthropods (Briggs & Kear, 1994a) but this is the first time that it has been observed in plant material from a terrestrial setting, where the factors controlling mineralisation may differ.

While phosphatisation has thus far been investigated principally in marine sediments, it is not surprising that this type of mineralisation also occurs in ancient cess pits. Soil solutions extracted from the York cess pit sediments were all mildly acidic (approximately pH 5), a condition under which apatite is relatively stable but calcium carbonate remains in solution. The relatively low pH in the cess pits can be explained by the accumulation of acidic by-products of decay, such as fulvic and humic acids produced during degradation of plant matter, and fatty acids released from soft tissues. The abundant organic matter in the ancient cess pits would have provided a source of phosphorus, with the necessary calcium supplied by shells and bones, in addition to lime thrown into the pits for sanitary purposes.

The elemental composition of the mineralised concretions recovered from the cess pits is an important indicator of the redox conditions under which phosphatisation took place. It is useful to compare the composition of the cess pit Samples with other phosphatic concretions since the elemental composition of a given concretion will vary according to the setting in which it formed. The Mn content of the cess pit

concretions is significantly greater than that of phosphatised concretions recovered from the Eocene London Clay (Allison, 1988b). Since Mn ions produced by Mn-reduction would be incorporated into the calcium phosphate as it formed, this suggests that Mn-reduction was the major degradation pathway in the sediment surrounding the concretions. This places their formation in a very specific position, as Mn-reduction occurs high in the sediment column, near the anoxic-oxic boundary below the sediment-water interface (Allison, 1990). This has the implication that fully reducing conditions are not required for phosphatisation to take place. The very high Fe concentration recorded in the concretion from the oldest cess pit (105) may be the result of decay in the Fe-reduction zone below the Mn-reduction zone. Although older sediments were more deeply buried through time, this does not necessarily imply a significant increase in burial depth; a switch to Fe-reduction as the dominant decay pathway would automatically follow depletion of Mn sources in the sediment. Only one of the other concretions (11) appears to have an iron content comparable to the London Clay concretions, suggesting that, in general, Fe-reduction was not a major decay process in the ancient cess pits during concretion formation. However, a Student's t-test failed to find a significant overall difference in iron concentration between the cess pit and London Clay concretions. Furthermore, evidence that significant Fe-reduction took place at some time during the history of the cess pits is provided by the soil solutions, which are typically depleted in iron relative to fresh water, and to modern woodland and sandy grassland soil solutions. Levels of Mn in the soil solutions are also generally lower than those in woodland and sandy grassland soil solutions. Although modern grassland clay soil solutions have lower Fe and Mn concentrations than those from the cess pits, comparison with the sandy cess pit sediments may be misleading; elemental interactions with clay

minerals present in the grassland clay may result in relatively low soil solution concentrations. Significant concentrations of Fe and Mn are also present in the phosphatised embryos of the Coppergate crab apple seeds, implying similar conditions of formation.

While apatite would have been relatively stable in the mildy acidic cess pit pore waters, its precipitation was limited to very localised areas. Phosphorus concentrations were presumably too low to allow apatite formation, except where PO_4^{3-} ions were concentrated in some way. Although frequent addition of organic matter to the cess pits would ensure burial within hours or days, the rarity of mineralised fossil remains in these deposits suggests that the closed conditions required for phosphatisation developed on a highly localised scale.

With the exception of faecal concretions, the crab apple pips are the only mineral replaced specimens recorded from Context 18529 of Coppergate. The bulk of the biological remains at Coppergate comprise well-preserved, waterlogged organics. Mineral replaced specimens are rare from the site as a whole and are limited to oat (*Avena* sp.) grains, field bean (*Vicia faba*) cotyledons and testa fragments, and sloe or plum (*Prunus* sp.) fruit stones, in addition to crab apple pips. All of these were recovered from faecal deposits and perhaps significantly, represent three of the most commonly mineral replaced plant remains recorded from 35 sites (comprising over 200 contexts) studied by the E. A. U. in recent years. Mineral replaced crab apple pips also occur frequently at these sites. The relative scarcity of mineralised material at Coppergate contrasts with other archaeological sites in which the bulk of the biological remains are mineralised and waterlogged organic material is relatively rare, e. g. Hamwic (Saxon Southampton; Girling & Kenward, 1986).

The intact organic seed coats may have allowed the crab apple seeds to act as ion sinks, accumulating high concentrations of phosphate ions

within their embryos as they decayed. It is clear from elemental analysis (ICP-AES; Table 2. 5.) that embryos contain insufficient phosphate to effect their own mineralisation, so that diffusion of ions into the seeds from an external source (presumably decaying faecal matter surrounding them) must be assumed. Presumably this process was driven by a concentration gradient, which would have prevented movement of the ions back out through the seed coat.

The blackberry endocarps show a similarly high level of organic preservation to the crab apple pips, with little evidence for seed coat decay, and yet they lack mineralised embryos. Similarly, the abundant *Prunus* stones in the pit remain intact and unmineralised. This may reflect differences in the permeability of the seed coats to sediment pore waters bearing the ions required for phosphatisation (Helbaek, 1969). *Rubus* and *Prunus* seeds are renowned for the hard, recalcitrant nature of their endocarps, while *Malus* seed coats are known to be permeable (Guppy, 1912). Hence, while decay is assumed to be widespread in the cess pit, the impermeability of the *Rubus* and *Prunus* endocarps would have created a barrier to the ions produced and prevented embryo mineralisation. Mineralised *Prunus* stones are known from other contexts on the Coppergate site and are the most commonly mineralised plant remains recorded from the archaeological sites studied to date by the E.A.U. This suggests that the conditions required for mineralisation typically develop at an advanced stage of decay, when such recalcitrant structures as plum stones are undergoing degradation. The high level of preservation shown by the Coppergate seed coats and endocarps analysed suggests that in deposits with low decay rates, more recalcitrant structures may remain relatively unaltered for many years following rapid decay of labile tissues. It is likely that extensive phosphatisation usually occurs in deposits in which seed coats and other resistant organic structures decay

more rapidly. Although background pore water ion levels are likely to be relatively high in cess pits and other organic deposits, in poorly degraded deposits like Coppergate the decay rate would generally be too low to allow widespread mineralisation. In this case, mineral replacement was restricted to crab apple embryos due to the permeable nature of their seed coats which allowed them to concentrate ions. In an organic deposit with a more rapid decay rate, these embryos would be totally degraded and mineralisation of tougher tissues such as seed coats would take place in tandem with their decay.

The presence of a mineralised *Centaurea* achene in one of the recently excavated cess pits appears to contradict this idea, since these propagules show dormancy, implying that their seed coats are impermeable. The coat of the achene may have been damaged in some way to allow mineralisation of the embryo. It is possible that the fruit was ingested, although the intact nature of the specimen makes it unlikely that it was milled with flour. The inclusion of the achene within a mineralised concretion may indicate that microbial decay activity was concentrated in the area immediately surrounding it, so that the coat was simply degraded, allowing access to its embryo.

In a similar way to the crab apple seed coats, the cuticles of the dipteran larvae and the earthworm epidermis would have acted as a barrier to ionic diffusion during the early stages of decay, allowing internal phosphatisation of these animals. Precipitation of an apatite layer on the outer cuticle and epidermis was presumably linked with the respiration of the microbes which colonise these outer surfaces after death.

Formation of phosphatic concretions within the sediment is less straight forward. In some cases, apatite precipitation has occurred along obvious horizontal planes in the sediment, and Kenward and Hall (1995) have noted that at some sites, mineralisation is prevalent at the edge of

cess pits. It is likely that high ion concentrations develop on any plane over which pore water drainage is impeded, promoting mineralisation. However, this does not explain the presence of isolated concretions which do not form part of any obvious hydrological interface. The relatively common occurrence of seeds, grains and arthropods within these concretions suggests another mode of formation. As faecal deposits, the majority of the organic matter in cess pit sediments comprises minute bran fragments with a relatively uniform distribution throughout the sediment. By implication, microbial respiratory activity would also be uniformly distributed, producing pore waters of similar ionic composition throughout the deposit. Where a seed or other large and easily decayed organic particle is present, microbial activity will be locally intensified, producing a peak in pore water PO_4^{3-} ions, which will potentially allow apatite formation.

2. 4. 1. 2. The timescale of phosphatisation

The tissues preserved in the phosphatised cess pit fossils give an indication of how long the phosphatisation process must have taken, as different tissues will clearly decay at different rates. Although the timescale of phosphatisation in ancient cess pits can only be accurately established by carrying out decay experiments under cess pit conditions, the results of previous experimental work investigating phosphatisation in marine settings can act as an approximate guide. The most labile tissues preserved in the mineralised invertebrates are muscle tissues in the dipteran larvae and earthworms, and blood vessels in one of the earthworms. Experimental decay of marine decapods (Briggs & Kear, 1994a; Briggs et al., 1993) resulted in the replacement of various soft tissues by calcium phosphate, including muscle fibres and sarcolemma, and eggs. In these shrimps, phosphatisation was initiated after two weeks

of anaerobic decay and continued for a further four weeks. A comparable timescale might be inferred for phosphatisation of the muscle tissues in the cess pit, with replication of the muscle fibres preserved in the larvae having been initiated within a couple of weeks of death. Although the earthworms had reached a more advanced stage of decay before phosphatisation was initiated, indicated by the fact that the muscle fibres are absent and only the sarcolemma which sheathed them were preserved, some of the experimentally decayed shrimps also reached this state from two weeks onwards. Phosphatised blood vessels have previously only been reported in the secondary lamellae of fish gills and in pterosaur wing membranes from the Santana Formation of Brazil (Martill, 1988, 1989), although fossilised blood cells were recovered from the bone marrow cavities of human skeletons from a Hellenistic (330 to ca. 150 years BC) desert burial in the Persian Gulf (Maat, 1991). Based on observations of gill decay in modern trout specimens, Martill estimated that phosphatisation of the Santana fish gills must have happened within five hours of death. However, the blood vessels preserved in the cess pit earthworm are isolated and represent the only evidence of structural preservation in that particular specimen, so a longer period of decay is likely before phosphatisation was initiated. It is unclear why the blood vessels were phosphatised while the muscles they were supplying were not. Unfortunately, the small size of the blood vessels meant that it was not possible to establish with certainty that they were indeed replicated in calcium phosphate, as is the surrounding matrix.

The phosphatised plant fossils studied comprise various propagules, in which structural preservation is generally restricted to the cell walls of endosperm tissue with rare replication of seed coats and cotyledon tissue. The cotyledon areas of the fossils were typically filled with mineralised spheres, but it is not clear whether these represent replicated nutrient

bodies or mineralised bacteria, or whether they are simply abiotic mineral spheres. Although there is no experimental work that can act as a guide to how long phosphatisation of seed embryos is likely to take, the decay of the cotyledons of the seed is likely to be rapid, as these comprise mainly food reserves that would be easily metabolisable by microbes. The timescale of embryo phosphatisation will ultimately be dictated by how soon after death the embryo is exposed to microbial attack. Plans for further work on the experimental decay of seeds are outlined in Chapter 5 section 5. 6. 2.

2. 4. 1. 3. Post-excavation mineralisation of stored sediments

A discussion of cess pit mineralisation would be incomplete without addressing the phenomenon of post-excavation concretion formation. It is not uncommon for mineralised concretions to form within organic-rich archaeological sediments during storage (Hall, *pers comm.*, 1998), and an example of this is the "stable manure" looked at in this study. It is likely that these sediments are still microbially active when they are excavated, so that they still contain viable microbial populations when they are put in storage. During storage, it is possible that microbial degradation of any organic matter present could continue and, given the fact that sediment pore waters within a plastic tub are totally restricted, their ionic concentrations will continue to rise as long as the microbes persist and respire, eventually allowing mineral precipitation provided sufficient ions are present in the storage vessel.

2. 4. 2. Preservation of organically-preserved fossils in ancient cess pits

2. 4. 2. 1. Propagules

SEM of fossil crab apple seed coats recovered from the Coppergate ancient cess pit revealed a very high level of structural preservation, with no obvious physical differences to distinguish them from modern specimens. Corncockle seed coats did look degraded relative to their modern counterparts but this was subtle and it was difficult to differentiate between the extent of degradation in different fossils specimens. Blackberry endocarps from Coppergate are indistinguishable from modern specimens. This apparent lack of diagenetic alteration was corroborated by pyrolysis-GC/MS of the seed coats/endocarps, which revealed only very minor chemical degradation. Pyrolysis markers for all original biomolecules were still present in the seed coat/endocarp pyrolysates.

The three seed species analysed all revealed different coat compositions. Only the composition of the blackberry endocarp is "typical" of angiosperms, comprising lignin and cellulose. The lignified blackberry endocarp yielded a pyrolysate virtually indistinguishable from the pyrolysate of a modern specimen, although minor cellulose degradation was suggested by an increase in some low molecular weight products.

The crab apple seed coats have a more unusual composition, interpreted as a tannin-cellulose complex. Markers for all original biomolecules are present in the pyrolysate for the Coppergate fossil specimens, including the hemicelluloses, which are relatively susceptible to decay. A decrease in the abundance of the major cellulose pyrolysis product (levoglucosan) in the fossil, and an increase in some of the low molecular weight carbohydrate markers, relative to modern crab apple seed coats suggest that carbohydrate degradation has begun, but the

persistence of hemicelluloses indicates that this has reached only a very early stage. Although the unusual seed coat composition has not affected crab apple pip preservation in the Coppergate cess pit, this deposit is considered to be relatively well preserved, as it yielded a very diverse fossil assemblage compared to the other cess pits studied. The impact of the non-lignified seed coat composition on preservation potential is revealed by the sub-fossil content of the other (presumably less well preserved) cess pit samples. Samples 15, 11, 64 and 105 all contain crab apple endocarp (core) but did not yield any seeds, implying that these have totally degraded. Hence, crab apple and any other species with tannin-cellulose seed coats have been selectively degraded from certain deposits, resulting in a preservationally biased sample of the original plant assemblage. It is not possible to predict whether or not tannin-cellulose seed coats will be preserved in a given deposit based simply on age, as the cess pit samples containing only crab apple endocarp range from the 4th to 16th Century, while the Coppergate sample dates from the 10th Century. The factors that determine decay rate (such as redox conditions and organic input) within a deposit dictate the level of preservational bias in the plant assemblage that it contains.

Pyrolysis of corncockle seed coats revealed that they also deviate from a lignin-cellulose composition. They comprise mainly proteins and polysaccharides, with tannins also present; lignin is present in minor amounts, if at all. Pyrolysis results suggested little variation in the extent of degradation of the various fossil seed coats, despite the large age range of the samples (spanning the 12th to 16th Centuries), so that the coats may apparently remain relatively unaltered for long periods of time. Quantitative analyses of the proteins and carbohydrates present in the fossil corncockle seed coats revealed differences in the amounts of these

biomolecules persisting in different fossil specimens (see **2. 3. 1. 4. 2.** & **2. 3. 1. 4. 3.**).

The presence of corncockle seed coats in samples which lack crab apple seed coats suggests that seed coats dominated by proteins and carbohydrates are more decay resistant than those comprising mainly tannins and carbohydrates. However, the fact that the oldest cess pit sample studied (dating from the 4th Century AD) lacks corncockle seed coats, while other fossil propagules (including lignified blackberry endocarps) are still present, may indicate that these coats also have a lower preservation potential than structures composed of lignin and cellulose (see van Bergen *et al.*, 1996), although this introduced plant was more uncommon in Roman than Medieval Britain. Furthermore, the fact that corncockle seed coats are food contaminants that usually find their way into cess pits within human faecal material may confer on them an enhanced preservation potential, compared with other seed coats with a similar composition. The presence of surrounding faecal material may protect the seed coats from decay, particularly where it becomes partially mineralised. The seed coats analysed in this study were recovered from unmineralised portions of sediment, but even where faecal material has not become mineralised, it may still act as a buffer zone for the seed coats within it, providing an easily digestible substrate for bacteria, so that the more recalcitrant seed coats will be exploited only when the nutrient capacity of the faecal material has been depleted or other factors become limiting. Hence, study of protein/carbohydrate/tannin seed coats that do not represent food items or contaminants is necessary to establish the intrinsic preservational potential of this category of seed coats.

2. 4. 2. 3. Possible reasons for differences in organic preservation between the different cess pits

In general, pyrograms of organically preserved remains (seed coats/endocarps, beetles and pupal cases) from the five cess pit samples suggested little variation in the quality of preservation in different pits. The pyrolysis products for all biomolecules detected in the modern specimens analysed for comparison were also present in all of the fossils, indicating that they were all relatively well preserved. Differences in the relative abundances of certain pyrolysis products in the pyrograms for different fossil samples suggested that they had undergone degradation to varying extents, but the overall range of preservation was relatively narrow.

Quantitative analysis of the protein and carbohydrate fractions of the corncockle seed coats revealed that there was variation in the concentrations of amino acids and monosaccharides detectable in the fossil samples, and these generally followed a similar trend, with the highest concentrations remaining in many cases in sample 64 or 11, decreasing down through 17, with sample 15 usually preserving the lowest concentrations. These results were only in partial agreement with observations made under the SEM, where the specimens from samples 64 and 15 looked relatively better morphologically preserved than samples 11 and 17. However, the brittle nature of the seed coats meant that only the testal surface could be observed and it was difficult to gauge with any confidence the relative preservational state of the different seed coats on this basis.

Although corncockle seed coats were absent from the oldest cess pit sample in this study (4th century), there does not appear to be a relationship between age and quality of preservation in the four pits that did yield corncockle. The samples in which the highest concentrations of

sugars and proteins were detected (64 and 11) are the oldest, dating from the 12th-13th and 13th-14th centuries, respectively. Conversely, sample 15, in which the lowest concentrations of amino acids and monosaccharides were detected, is one of the younger samples (16th century). It is clear that there is variation in the decay rates within different cess pits, and this is likely to be determined by a combination of different parameters, such as degree of waterlogging and amount of organic material present.

2. 4. 2. 2. Insects

The insect cuticles recovered from the ancient cess pits comprised beetle elytra and dipteran pupal cases. Those cuticles examined under SEM displayed a consistently high level of structural preservation, although some separation of chitin fibrils was observed in the procuticle of one beetle elytron, suggesting some degradation of the intervening protein matrix. The extent of chemical degradation of the fossil cuticles was assessed through comparison of their pyrograms with those derived from fresh and decayed reference cuticles (weevil and horn worm pupal exuviae analysed by the author and beetle and shrimp cuticles analysed by Stankiewicz *et al.*, 1996, 1998b and Duncan, 1997). If it is assumed that the relative abundances of compounds generated by pyrolysis are a fairly accurate indicator of preservation state of the source molecules (see Flannery *et al*, 1999), all of the cess pit fossil cuticles analysed show minimal apparent chemical degradation, as the full range of protein and chitin pyrolysis markers are present. This suggests that they represent a preservational state equivalent to that of less than 2 weeks decayed mantis shrimp *Neogonodactylus oerstedii* cuticle (Stankiewicz *et al.*, 1998b); certain protein moieties were no longer detectable in the shrimp cuticle pyrolysate generated after 2 weeks of decay. Degradation proceeded

much more slowly in the *Manduca sexta* decay experiment, and on the basis of relative abundances of pyrolysis products, the majority of cess pit fossil cuticles probably represent a stage of degradation beyond that reached in the final (64 weeks decayed) sample. Degradation of insect cuticles clearly proceeds much more slowly in the aerobic, fresh water conditions used in the *Manduca* laboratory experiment and the *Tenebrio molitor* pond experiment than decay of crustacean cuticle in anaerobic marine conditions. This reflects the sclerotised nature of certain insect cuticles, versus the non-sclerotised mineralised cuticles of crustaceans. Another factor may be that the microbes responsible for chitin decay operate mainly under anaerobic conditions, and that it took some weeks for the oxygen present in the *Manduca* experimental vessels to become depleted. Despite the slow decay rate, the *Manduca* experiment is useful for illuminating the preservational state of the cess pit fossils, since they too have reached a relatively retarded degradation state. Elemental analysis of mineralised concretions and sediments from the cess pits suggested that redox conditions were borderline aerobic/anaerobic, so it is possible that the cess pits were not generally anaerobic enough to allow rapid microbial degradation of the cuticles. However, characteristics of these particular cuticle types are likely to have been most influential in their preservation, conferring on them a greater decay resistance than other insect cuticle remains. The cess pit samples from which the analysed cuticles were recovered yielded no other types of insect remains, and beetles and fly puparia are likely to represent only a fraction of the entire insect assemblage originally deposited in the pits. Hence, beetle elytra and fly puparia must have a higher preservation potential than other insect cuticle types. This is in agreement with previous studies which concluded that thick, heavily sclerotised beetle elytra are much more recalcitrant than other insect remains, resulting in their

preservation in Quaternary and Tertiary deposits where no other insect cuticles persist (Stankiewicz *et al.*, 1997b; Duncan, 1997; Flannery, 2000). The cuticles of dipteran pupae also undergo sclerotisation during puparia formation, presumably conferring on them a similar level of robustness.

It is difficult to compare the extent of degradation of the different fossil cuticles in the absence of quantitative chemical analyses. However, the variation in the abundance of acetamide between samples presumably reflects differences in the extent of chitin degradation that has taken place in different fossil cuticles. The pyrolysates of the pupal cases and sample 17 beetle elytron retain relatively abundant acetamide but this compound has greatly diminished in the pyrolysates for the beetle elytra from sample 15 and 11, suggesting that chitin degradation has begun. Although the preservational state of the proteins in the cuticles is more difficult to assess, the relative abundances of the pyrolysis products suggest that these elytra have undergone more significant protein degradation than the other cuticles. The fact that sample 15 is the same age as the better preserved specimens (16th Century) suggests that, as expected, age is not a significant factor in preservation. This is corroborated by the fact that the Beverley sample (11) is one to two centuries older than the comparably preserved sample 15, and the 13th-14th Century sample (64) did not yield any insect remains at all, while beetle remains were recovered from the oldest (4th Century) sample.

2. 4. 3. Bone fossilisation in ancient cess pits

The extent of bone fossilisation in the ancient cess pits was quantified by carrying out XRD analysis of the mineral (hydroxyapatite) portion of the bones and calculating a Crystallinity Index (C. I.). Human bones (ribs) from graves at Barton-on-Humber, dating from the 10th-11th and 18th-19th Century, were analysed to allow comparison with better-drained, less

organic deposits. Bones from the cess pits produced X-ray diffractograms (Figure 2. 45. (b)) which were virtually indistinguishable from those of fresh bones, in contrast to those of the Barton graveyard bones, which displayed three sharp, distinct apatite maxima. Plotting the C. I. for all of the bones analysed produced a graph in which the Barton-on-Humber bones occupied a consistently lower position than the cess pit bones. A Student's t-test of the data confirmed a highly significant difference ($p < 0.001$) between the C. I. s of the two deposit types. The Barton bones have clearly undergone much more hydroxyapatite alteration, in contrast to the negligible alteration of the cess pit bones.

An increase in the distinctness and sharpness of the three main apatite maxima on X-ray diffractograms has long been recognised as evidence for bones becoming increasingly "fossilised" (Bartsiokas & Middleton, 1992). The reasons for this increase in sharpness are thought to include an increase in the size and perfection of the apatite crystallites as they dissolve and recrystallise (Hassan *et al.*, 1977; Kyle, 1986; Schoeninger *et al.*, 1989) or as geological apatite precipitates on the bone tissue (Schoeninger, 1982), and ionic exchange with fluorine (Perinet *et al.*, 1975). Hedges *et al.* (1995) identified the affect of major hydrological regimes on the rate of bone dissolution, and these have been mathematically modelled by Hedges *et al.* (1995). Although the concentration of organics, even in modern bone, is thought to be too low to affect crystallinity (Termine & Posner, 1967), the intimate arrangement of collagen fibres and apatite crystallites may result in a mutually protecting system, in which the protein and mineral portions shield each other from microbial degradation and dissolution respectively (Collins, pers comm., 1999). Hence, alteration of hydroxyapatite only proceeds once significant organic decay has taken place.

Formation of authigenic apatite was observed to some degree in all of the cess pit samples studied, so a decrease in the C. I. s of the cess pit bones might be predicted, due to precipitation of additional apatite on their surfaces and within their pores. Furthermore, Hedges *et al.* (1995) showed that the rate of hydroxyapatite dissolution at pH 5, the pH of cess pit pore waters, is two orders of magnitude greater than that at neutral pH. Hedges *et al.* (1995) recognised three major hydrological categories, each associated with a distinct pattern of bone dissolution. The ancient cess pits probably correspond most closely to *diffusive environments,* where the sediment is waterlogged and there is no net flow of water into or out of bones. The fastest rates of bone dissolution were predicted in these environments, where dissolution occurs mainly through the movement of solutes (in their model, Ca^{2+} ions) along diffusion gradients. Under these conditions, and assuming a zero Ca^{2+} concentration in the ground water, an entire human leg bone should disappear within 0.13 years at pH 5! Assuming a more typical ground water Ca^{2+} concentration, the predicted residence times of bones in the sediment is increased by four orders of magnitude, which seems more consistent with observations of archaeological and palaeontological specimens. The negligible hydroxyapatite alteration of the cess pit bones may be explained by the high ion concentrations in the ground water and by the generally high level of organic preservation observed in the pits. Precipitation of authigenic apatite in the cess pits implies localised saturation of the ground water with respect to Ca^{2+} and PO_4^{3-} ions. If the cess pits are assumed to be waterlogged for the majority of the time, hydroxyapatite alteration in any bones present will occur principally through diffusion, a process which will be very slow in groundwaters with high ionic concentrations. Any authigenic apatite precipitated on and in the fossil bone is unlikely to greatly alter C. I. if the bone mineral itself remains

largely unaltered. Furthermore, the persistence of relatively well-preserved proteins in seed coats and beetle elytra from the cess pits suggests that the organic content of the bones (principally the protein collagen) also remains intact. As suggested by Collins (1999, *pers comm.*) the collagen in the cess pit bones may have protected the hydroxyapatite crystallites from alteration.

The significant difference between the C. I. s of the cess pit and Barton-on-Humber bones may also relate to hydrological properties of the deposits. The Barton-on-Humber graveyard represents a better-drained sediment, although half of the bones studied were from coffined burials which were presumably more hydrologically restricted. Water movements at Barton-on-Humber were probably dominated by the downward infiltration of rain water through the soil. Although this would have provided more sporadic opportunities for hydroxyapatite dissolution, this process is unlikely to have been impeded by the groundwaters being saturated with Ca^{2+} and PO_4^{3-} ions. Evidence for the importance of water movements in hydroxyapatite diagenesis of the Barton bones is provided by the different C. I. values obtained for the coffined and non-coffined skeletons at the site. The C. I. values of coffined bones are significantly higher than those of non-coffined bones (Student's t-test; $p <0.001$), indicating that they have undergone less hydroxyapatite alteration. This result was obtained for the bones from each of the two age groups separately ($p < 0. 05$ for 10th-11th Century; $p < 0.001$ for 18th-19th Century) and for pooled data for all of the bones ($p < 0. 001$). It is likely that the presence of a coffin restricted water flow around the bones, so that eventually the ionic concentrations of the sediment pore waters around the bones in the coffin reached a level high enough to slow down the dissolution rate of the bones.

The results of this study, in which archaeological bones deposited in ancient cess pits showed only negligible hydroxyapatite alteration when compared with bones from a graveyard, is in agreement with previous studies (e. g. see Hedges *et al.*, 1995). Despite the much greater age of some of the cess pit bones relative to the bones from the Barton-on-Humber graveyard, the latter are much more diagenetically altered, demonstrating that the characteristics of the burial environment and not age are important in determining the extent of hydroxyapatite alteration.

CHAPTER 3. PHOSPHATISED SEEDS AND ROOTS FROM A LATE BRONZE AGE MIDDEN AT POTTERNE, WILTSHIRE.

3. 1. Introduction

3. 1. 1. Taxonomic bias in the tissues mineralised at Potterne and aims of this study

The importance of phosphatisation in preserving plant remains in archaeological deposits was first recognised by Green (1979) and, in recent years, environmental archaeologists have noted the varying susceptibility of different taxa and tissues to this mineralisation process. However, there have been no studies aimed specifically at establishing the basis of this variation and its implications for bias in mineralised assemblages. This may be due in part to the limited taxonomic range of typical phosphatised plant assemblages; the vast majority of archaeological deposits which yield phosphatised remains are human faecal deposits such as cess pits and garderobes, and they yield plant assemblages that are heavily biased towards edible taxa. For example, in his survey of preservation in Medieval urban deposits in southern England, Green (1991) established that 90% of the mineralised plants recovered are orchard crops.

The Late Bronze Age midden at Potterne provides a rare opportunity to study a much wider range of mineralised plant taxa (64 genera/species from 29 families), which are almost exclusively weeds which grew on the midden itself or in the surrounding area, rather than edible plants brought onto the site for consumption (Carruthers, 2000). In her study of the mineralised Potterne plants, Carruthers (2000) recognised that the seeds which make up the bulk of the assemblage show taxonomic variation in the tissues that are mineralised, e. g. some species are always represented by both mineralised seed coats and embryos, while in other

species, only the embryo is mineralised. In a small number of species, such as elder (*Sambucus nigra*), seeds are mineralised both with and without their seed coats. In two species (*Carex* sp. and *Eleocharis* sp.), only a cell layer in the lower seed coat is mineralised along with the embryo. Mineralised root fragments, straw and rush fragments are also present, as well as soft-bodied invertebrates such as fly pupae, earthworm cocoons and an earthworm embryo (Piearce *et al.*, 1990, 1992). The mineralised roots are apparently exclusively those of dicotyledonous angiosperms, which suggests the presence of a taphonomic filter that excluded the roots of monocotyledons, as this major group of angiosperms is represented by various seeds at Potterne, at least some of which are likely to have been growing and therefore rooted on the midden.

The aim of this study was to discover the basis of the taxonomic variation recognised by Carruthers (2000) in the plant tissues phosphatised in the Potterne midden. Previous workers have suggested that structural features of the seed coat, such as degree of permeability and cell wall thickening, may dictate the extent to which seed tissues are mineralised (Green, 1979; Helbaek, 1969; Carruthers, 2000). Furthermore, study of seeds from a cess pit at Coppergate in York (Chapter 2) suggested that seed coat permeability was the factor determining whether the embryo of a given seed species was mineralised, at least in deposits with relatively limited mineralisation. However, there is also variation in the chemical composition of coats of different seed species, which results in significantly different decay rates (see Chapters 1 & 2). Therefore, this study considers both structural and compositional factors by looking at the structure of fossil and modern seed coats, and the seed coat composition of modern reference specimens. A similar approach is used to investigate the bias in favour of dicotyledonous roots in the Potterne

assemblage. Since the taxonomic identity of the roots is unknown, it was not possible to examine their modern counterparts. Hence, general information on root anatomy, composition and behaviour in the literature was used to interpret their preservation.

3. 1. 2. The Potterne midden

Potterne is situated near Devizes in Wiltshire, and a major feature of this Late Bronze Age occupation site is a midden which covers an area of approximately 3. 5 hectares, reaching a maximum thickness of 2 m (Carruthers, 2000). A small part of the midden was excavated by members of the Trust for Wessex Archaeology in 1983-1984, including sampling of sediment columns through the entire depth of the deposit. This revealed that mineralisation was prevalent throughout the midden and also in the soil beneath it, including a mineralised hard-pan at its base. The pre-midden occupation soil was anomalously organic, attributed to long-term animal herding on the site, which is also thought to have resulted in the formation of the hard-pan due to compaction which impeded drainage (Macphail, 2000). The base of the deposit was radiocarbon dated to the 15th century B.C. (uncalibrated) and may have been in use until the 6th century B.C. (uncalibrated radiocarbon date), spanning the Middle and Late Bronze Ages. A full description of the archaeology of the Potterne site can be found in Gingell & Lawson (1984) and Lawson & Gingell (1985).

3. 1. 3. The phosphatised plant assemblages from Potterne

Mineralised plant remains were found throughout the depth of the deposit, in both the midden sediments and in the underlying pre-midden occupation soil (Carruthers, 2000; Figures 3. 1. & 3. 2.). The

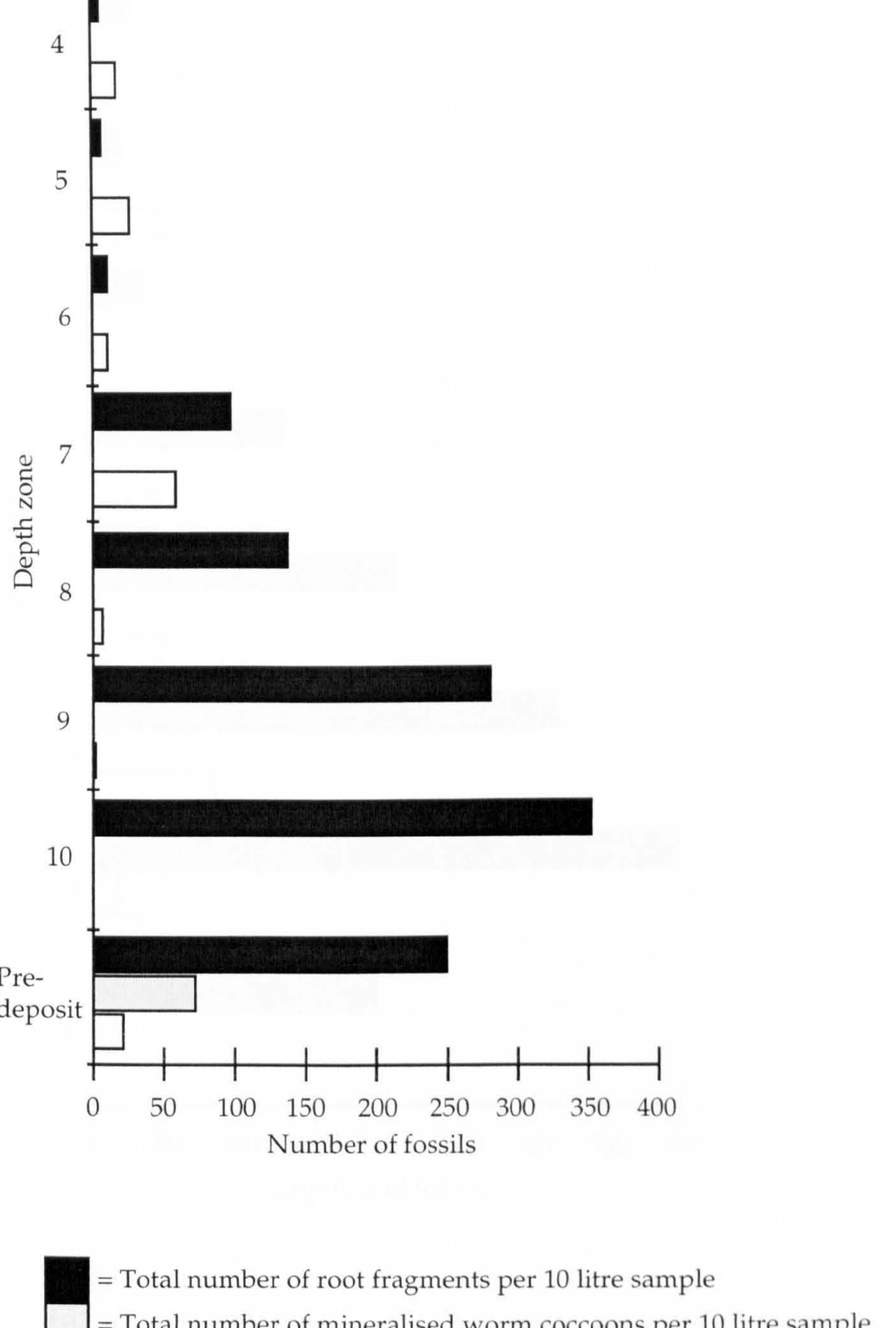


Figure 3.1. Numbers of mineralised root fragments, worm coccoons and seeds recovered from different depth zones of the Potterne midden. Depth increases from zone 4 down to the pre-deposit layer. After Carruthers (2000).

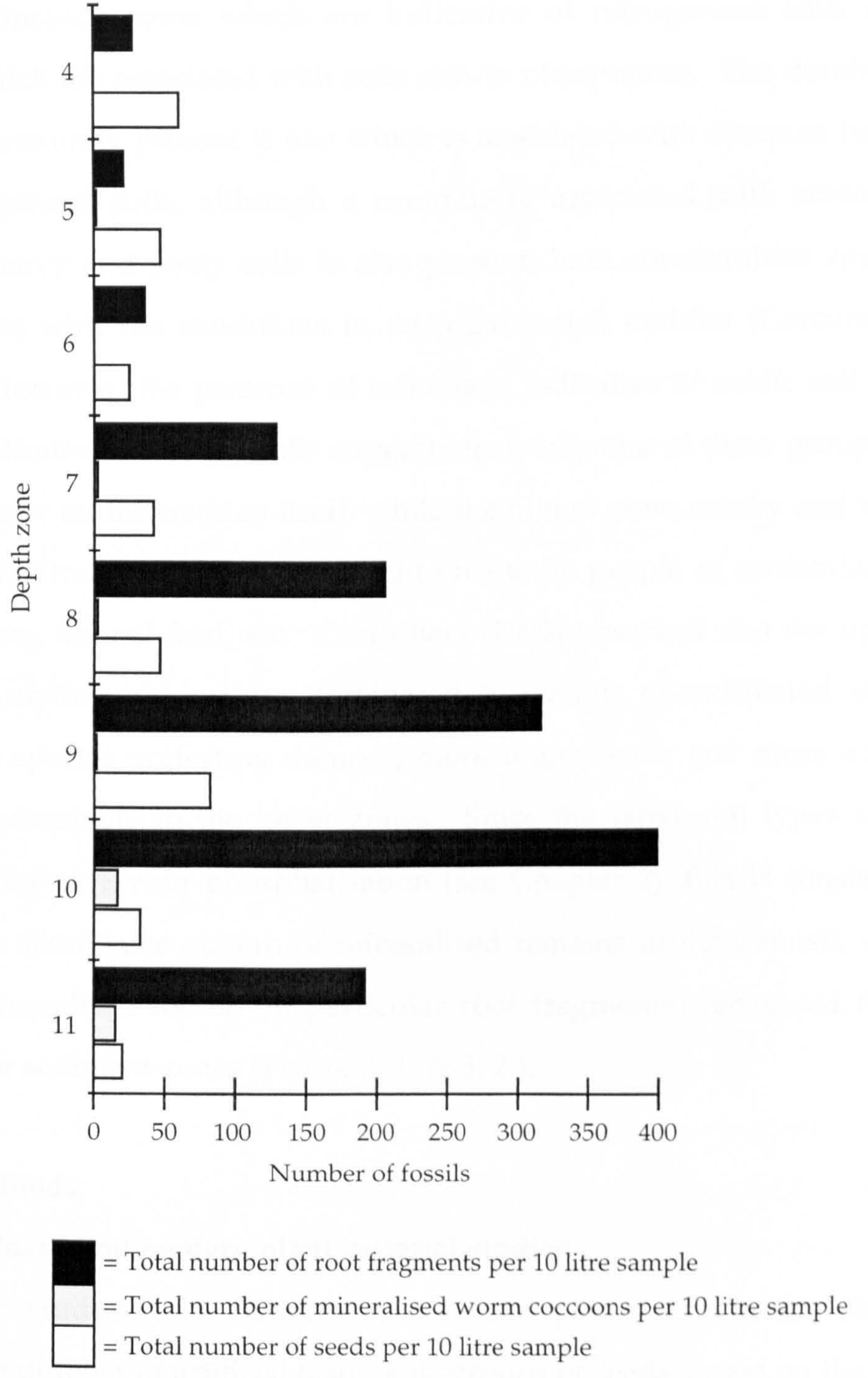


Figure 3. 2. Numbers of mineralised root fragments, worm coccoons and seeds recovered from different depth zones of the Potterne midden. Depth increases in from zone 4 down to zone 11. After Carruthers (2000).

majority of the mineralised seeds present in the midden are thought to represent the vegetation that was growing on it and, as such, may give an indication of the characteristics of the midden soil. The plant taxa present include some which are indicative of nitrogenous soils and some which are associated with soils rich in phosphorus. The dominant plant community present is one which is associated with compost heaps or nitrogenous soils, although a community associated with acidic or damp, heavy and peaty soils is also present; both communities appear consistent with the conditions in an organic-rich midden (Carruthers, 2000). However, the presence of some taxa indicative of acidic soil and some indicative of chalky soils suggests that only one of these groups of plants grew on the midden itself, while the others grew nearby and their seeds were transported in, or brought on site by people as contaminants of bedding, animal feed, etc. Carruthers (2000) observed that the upper regions of the midden are dominated by weeds of cultivated soils, whereas species preferring damper, more organic-rich and more acidic soils predominate in the lower zones. Since the latter soil types seem more likely to favour phosphatisation (see Chapter 2), this is consistent with the abundance pattern of mineralised remains in the deposit, with more mineralised fossils (in particular root fragments) recovered from the lower sediment zones (Figure 3. 1. & 3. 2.).

3. 2. Methods

3. 2. 1. Fossil and modern plant material studied

In her study of the Potterne mineralised plants, Carruthers (2000) created a number of artificial taxonomic groups of seeds, based on the fact that some closely-related taxa are indistinguishable in a mineralised state (usually because the seed coat is absent, resulting in very similar naked embryos). Identification of the Potterne seeds was carried out through

comparison with a modern reference collection, and it was often necessary to remove the coats from the modern seeds to reveal features of the embryo. Although the majority of the Potterne seeds lack coats, in some rare cases identification to species level is more straightforward because the seed coat is mineralised along with the embryo. Preservation between these two extremes occurs in the seeds of *Carex* sp. and *Eleocharis* sp., where the outermost mineralised layer is a membrane in the lower region of the seed coat. To investigate the basis of this taxonomic variation in mineralisation, examples of Potterne mineralised seeds with (*Urtica urens*) and without (Chenopodiaceae, *Hyoscyamus niger* and *Brassica/Sinapis* sp.) intact seed coats were studied, in addition to *Carex* sp. Modern representatives of each taxon (small nettle: *Urtica urens*; henbane: *Hyoscyamus niger*; club sedge: *Carex buxbaumii*; fat hen: *Chenopodium album* and black mustard: *Brassica nigra*) were analysed to aid interpretation of the fossils. Some of the mineralised roots were also examined.

3.2.2. SEM

To establish the nature of mineralisation of the fossil tissues (i.e. replacement, coating or infilling), the Potterne seeds and roots were mounted both entire and fragmented onto aluminium stubs using gold dag adhesive. Interpretation of the mineralised textures seen in the Potterne seeds was aided by SEM of their modern equivalents, which were freeze-dried and mounted as entire and sectioned specimens on aluminium stubs using gold dag adhesive.

3.2.3. py-GC/MS

To investigate the role of seed coat composition in determining the nature of seed mineralisation, the coats of modern examples of all of the

mineralised taxa studied were analysed using py-GC/MS. The coats were removed mechanically from the seeds, freeze-dried and crushed to a powder using a pestle and mortar. Solvent extraction was then carried out using DCM and MeOH (in the ratios 1:1, 2:1 and 1:0 v/v) to remove solvent soluble contaminants introduced during handling of the seeds. The samples were pyrolysed in a flow of helium at 610°C for 10 seconds. The GC was kept isothermal at 35°C for 5 minutes, and then increased at a rate of 5°C/min to 310°C. Finally, the oven was held at 310°C for 10 minutes.

3. 3. Results

3. 3. 1. Macroscopic appearance of fossils

The Potterne seeds and their modern equivalents were examined under the binocular light microscope, before being subjected to SEM. Due to difficulties in obtaining consistently clear images of the seeds under the light microscope, the surface features of some of the seed are illustrated using Scanning Electron Micrographs instead of light micrographs, which show the same features apart from the colours of the coats.

The surfaces of modern examples of *Urtica urens* (small nettle) seeds are covered with red spots which show slight relief (Figure 3. 3. A). The Potterne fossil specimens are amber-brown with no red spots, although a dimply surface relief is retained (Figure 3. 3. B). In places, the fossil seeds are beige in colour, apparently where the seed coat has flaked off to reveal the embryo. Fat hen (*Chenopodium album*) specimens look very different in their fossil and modern states. The fresh seeds have a very shiny, jet black seed coat (Figure 3. 3. C), whereas the Potterne Chenopodiaceae seeds are beige and traces of cell walls give them some relief in places (Figure 3. 3. D). In the modern *Carex buxbaumii* (club

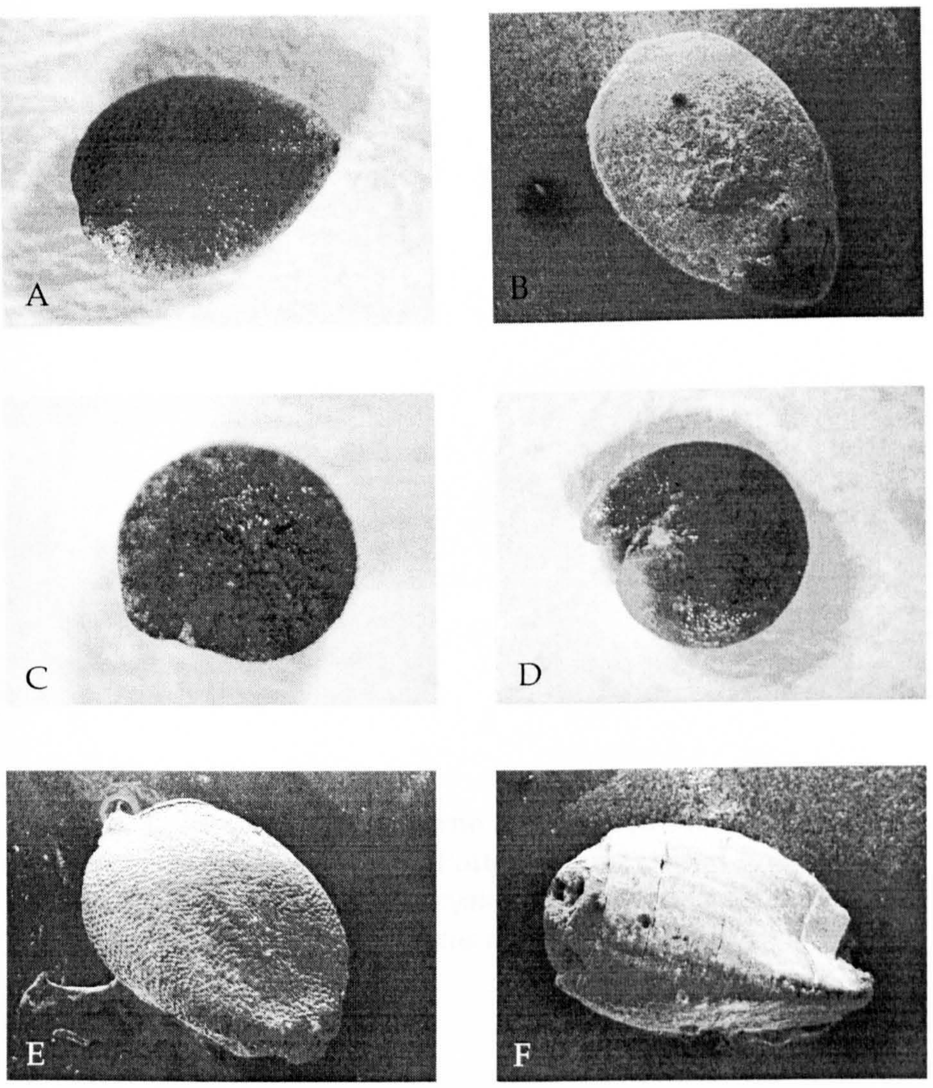


Figure 3. 3. Modern and Potterne mineralised seeds. A. Modern *Urtica urens* seed (x 200). B. Potterne mineralised *Urtica urens* seed (x 280). C. Modern *Chenopodium album* seed (x 250). D. Potterne mineralised *Chenopodium* sp. seed (x 250). D. Modern *Carex buxbaumii* seed (x 230). E. Potterne mineralised *Carex* sp. seed (x 220).

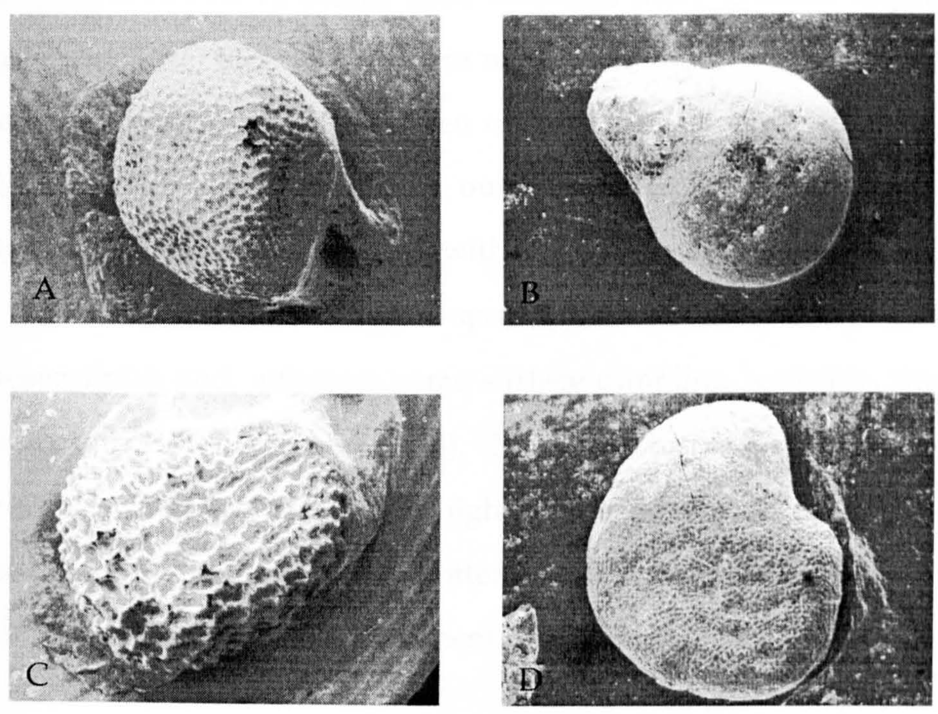


Figure 3. 4. Modern and Potterne mineralised seeds. A. Modern *Brassica nigra* seed (x 230). B. Potterne mineralised *Brassica* sp. seed (x 230). C. Modern *Hyoscyamus niger* seed (x 330). D. Potterne mineralised *Hyoscyamus niger* seed (x 330).

sedge) seeds, the outer seed coat surface is dark brown and the outlines of cell walls give them clear relief (Figure 3. 3. E). Potterne sedge specimens are purple-brown in colour and, although there is some impression of surface texture, the cell walls are not clearly evident (Figure 3. 3. F). In one specimen which was broken open, white mineralised material was visible within a purple-brown outer "shell". Black mustard (*Brassica nigra*) seeds are plum-coloured with a reticulate surface pattern (Figure 3. 4. A). Their fossil counterparts sport a more mundane beige to caramel-brown finish and, although some surface dimpling is visible, this is on a much finer scale (Figure 3. 4. B). Modern *Hyoscyamus niger* (Henbane) seeds are cream-coloured with high relief exteriors (Figure 3. 4. C), while the cream to amber coloured Potterne specimens show a slight dimpling but no significant surface ornamentation (Figure 3. 4. D).

3. 3. 2. Microscopic appearance

3. 3. 2. 1. Interpretation of mineralised fabrics seen in Potterne seeds

Under SEM, the Potterne fossil specimens of Chenopodiaceae, *Hyoscyamus niger* and *Brassica/Sinapis arvensis* seeds share a similar surface relief, although their overall shapes are distinct. All display an ornamentation of gentle, low-relief bumps (Figures 3. 5. A, C & E), which is interpreted as the outer membrane of the embryo through comparison with modern reference specimens (Figures 3. 5. B, D & F). This interpretation is confirmed by the presence of spherical mineralised bodies within the ornamented membranes, which closely resemble the nutrient bodies found within modern seed cotyledons (Figure 3. 6.). The impression of cell walls on one of the Chenopodiaceae seeds examined under the light microscope (see **3. 3. 1.**) suggests that there is limited endosperm preservation on some seeds.

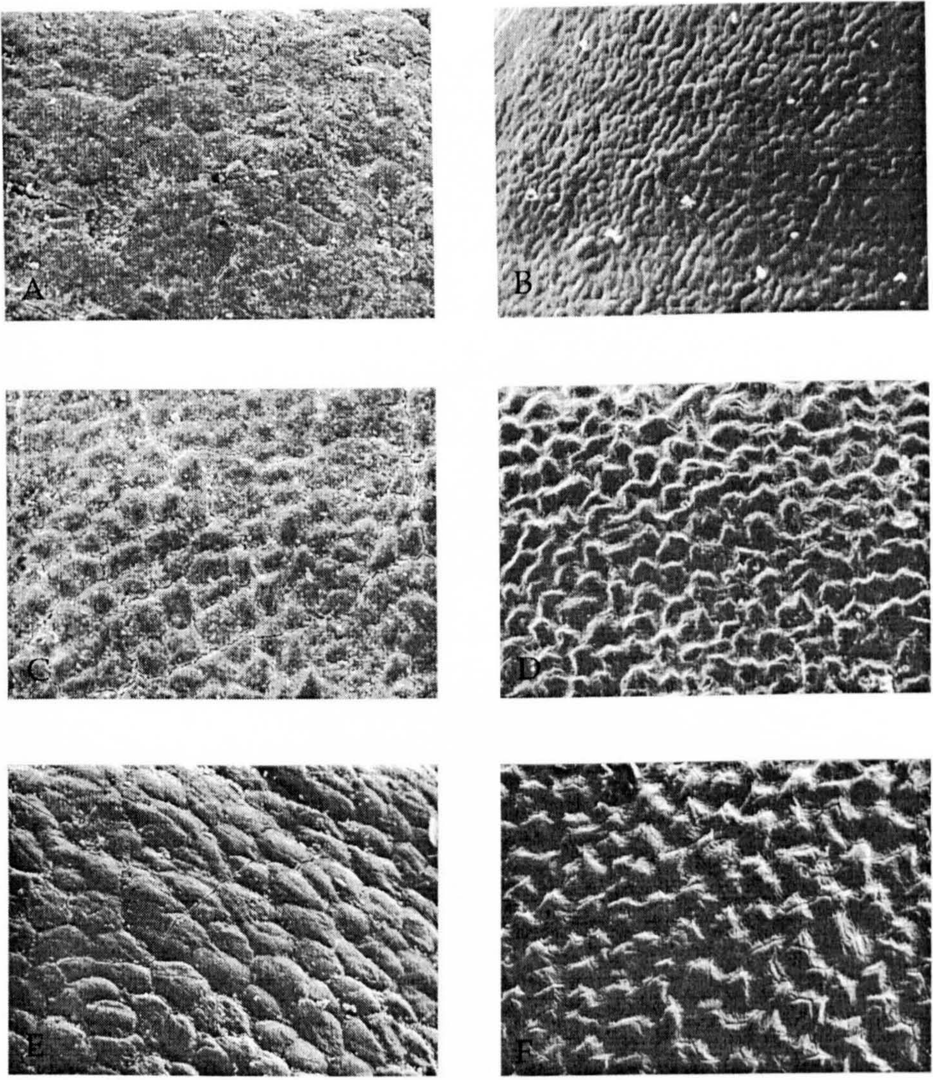


Figure 3. 5. Outer membranes of cotyledons in Potterne mineralised and modern seeds. A. Outer cotyledon membrane of mineralised *Chenopodium* sp. seed from Potterne (x 1600). B. Outer cotyledon membrane of modern *Chenopodium album* seed (x 4000). C. Outer cotyledon membrane of mineralised *Hyoscyamus niger* seed from Potterne (x 1600). D. Outer cotyledon membrane of modern *Hyoscyamus niger* seed (x 1500). E. Outer cotyledon membrane of mineralised *Brassica* sp. seed from Potterne (x 1200). F. Outer cotyledon membrane of modern *Brassica nigra* seed (x 1600).

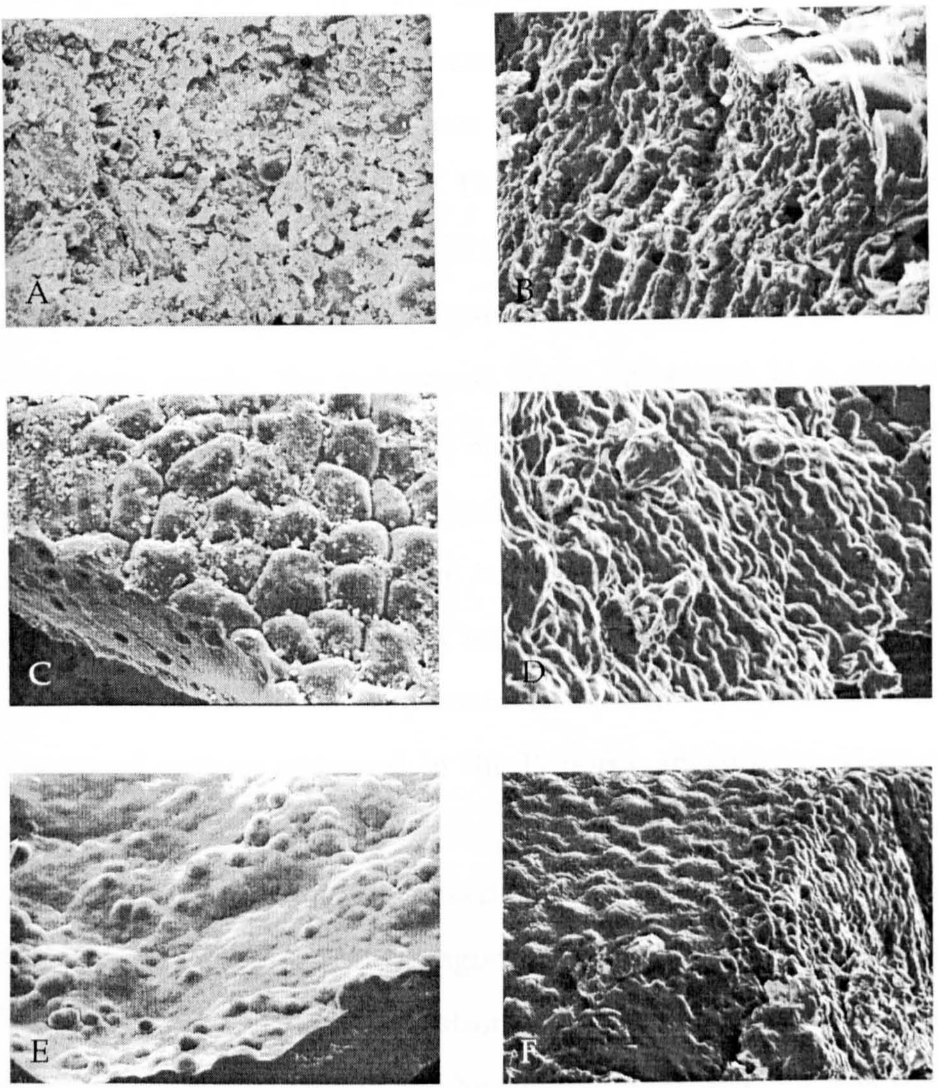


Figure 3. 6. Fabrics of cotyledon interiors in Potterne mineralised seeds and modern seeds. A. Internal fabric of Potterne mineralised *Chenopodium* sp. seed cotyledon (x 3800). B. Internal fabric of modern *Chenopodium album* seed cotyledon (x 2700). C. Fabric of outer cotyledon membrane and cotyledon interior in Potterne mineralised *Hyoscyamus niger* seed (x 2700). D. Internal fabric of modern *Hyoscyamus niger* seed cotyledon (x 3400). E. Internal fabric of cotyledon of mineralised Potterne *Brassica* sp. seed (x 2000). F. Outer membrane and interior fabric of modern *Brassica nigra* seed (x 2000).

Some *Urtica urens* fossils retain patches of the seed coat in addition to the enclosed embryo. A number of different cell layers are evident under SEM (Figure 3. 7.). The outermost layer preserved (retained at least partially in about fifty percent of the specimens studied) appears virtually structureless in surface view but in section, lineations are faintly visible in this thin layer. This is interpreted as the thin, relatively undifferentiated seed coat of *Urtica urens* through comparison with modern reference specimens (Figure 3. 7. A). In the remaining Potterne *Urtica urens* seeds, the outermost layer preserved is a meshwork of hexagonal cell walls (Figure 3. 8. A) but it is not clear whether this represents a layer in the lower seed coat or the endosperm tissue. When viewed from the underside, the base of the modern *Urtica urens* seed coat displays a layer of relatively low relief hexagonal cell walls (Figure 3. 8. C), whose mineral replacement could create the hexagonal mineralised pattern observed in the Potterne specimens. However, it is more likely that this represents mineralised endosperm, the tissue immediately underlying the seed coat, which in modern specimens consists of very high relief hexagonal cell walls containing starch grains (Figure 3. 8. B). This assumption is based on the fact that in some Potterne specimens, gaps in the hexagonal layer reveal a less rigid, more linear structure, interpreted as the outer membrane of the cotyledons (Figures 3. 8. E & F), confirming that the hexagons represent endosperm cell walls.

In the majority of Potterne *Carex* seeds examined under SEM, the outer-most layer preserved comprises a meshwork of elongate cell walls, interpreted as the endosperm tissue (Figures 3. 9. A & B). However, one of the specimens examined preserves patches of an additional tissue layer consisting of long parallel mineralised rods (Figure 3. 9. C). These are interpreted as infillings of the sclerenchymous cells in the base of the

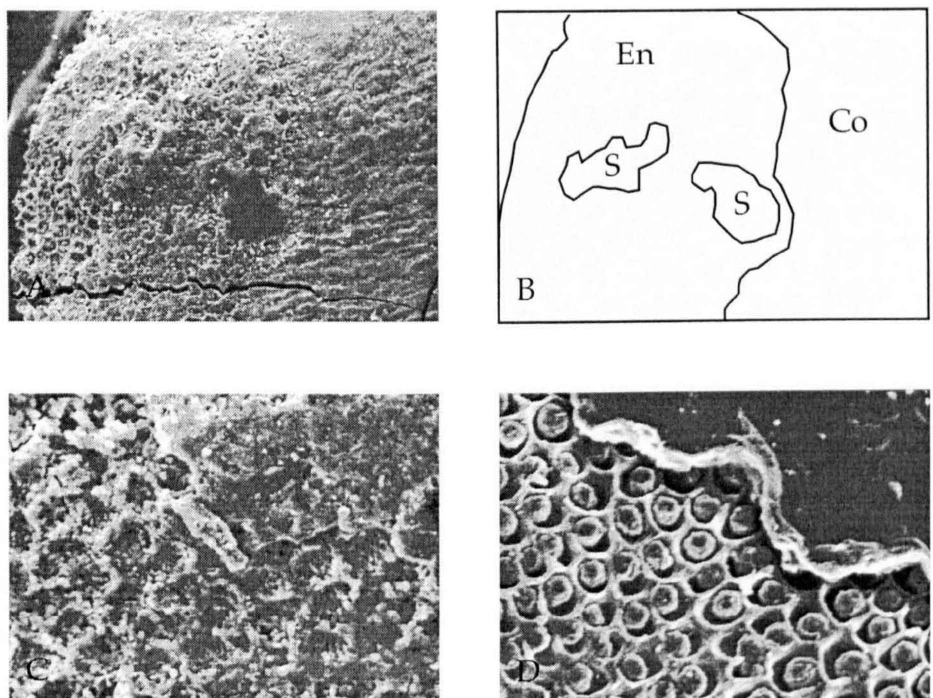


Figure 3. 7. Textures preserved in mineralised *Urtica urens* seeds from Potterne. A. Surface of mineralised *Urtica urens* seed showing seed coat, underlying endosperm tissue and cotyledon outer membrane (x 1000). B. Summary diagram of A. C. Mineralised *Urtica urens* seed showing fragment of seed coat (top right corner of picture) overlying hexagonal cells of the endosperm tissue (x 3700). D. Modern *Urtica urens* seed showing hexagonal cells of endosperm tissue and overlying seed coat (x 3300).

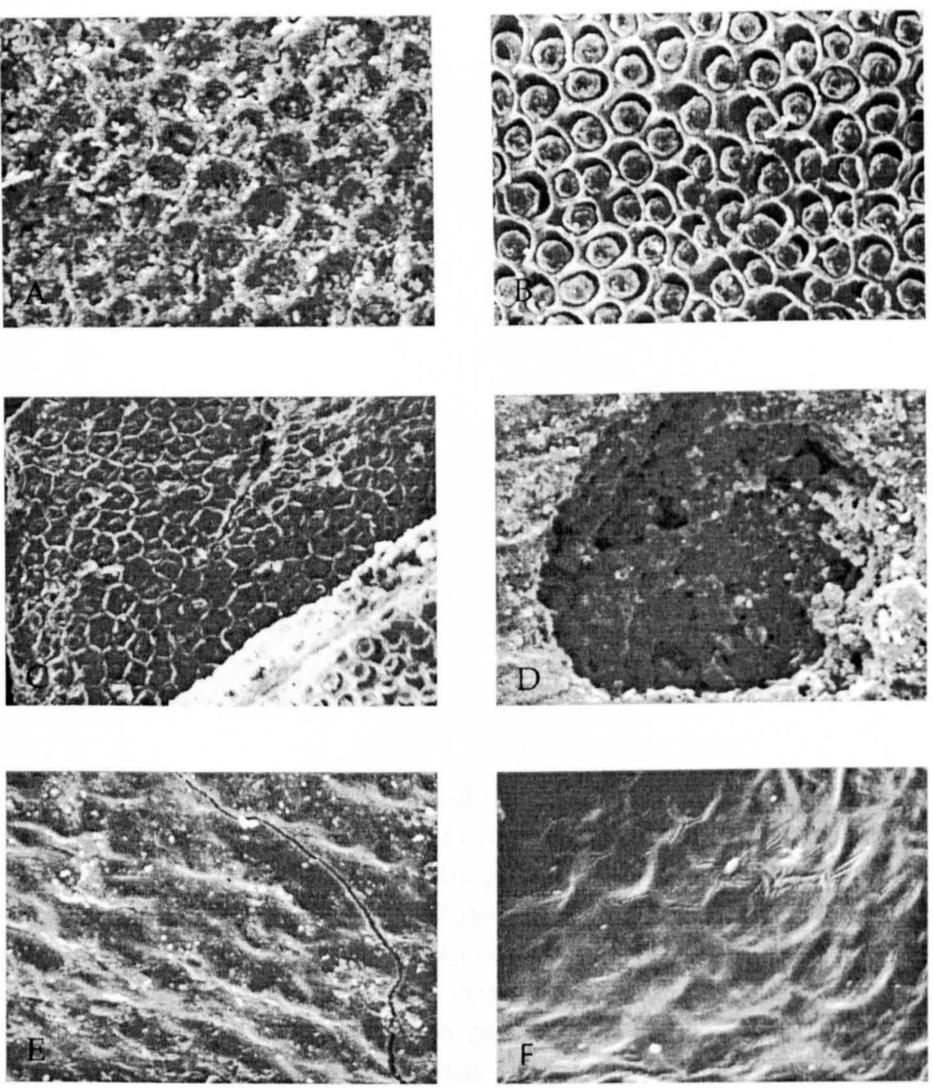


Figure 3. 8. Textures preserved in mineralised *Urtica urens* seeds from Potterne. A. Hexagonal cell walls preserved beneath the seed coat in mineralised *Urtica urens* seeds (x 3800). B. Hexagonal endosperm cells in modern *Urtica urens* seeds (x 3800). C. Layer of hexagonal cells at base of modern *Urtica urens* seed coat (x 2200). D. Gap in mineralised *Urtica urens* seed cotyledon outer membrane, showing spherical structures inside (x 3300). E. Outer cotyledon membrane in mineralised *Urtica urens* seed (x 2000). F. outer cotyledon membrane of modern *Urtica urens* seed (x 1700).

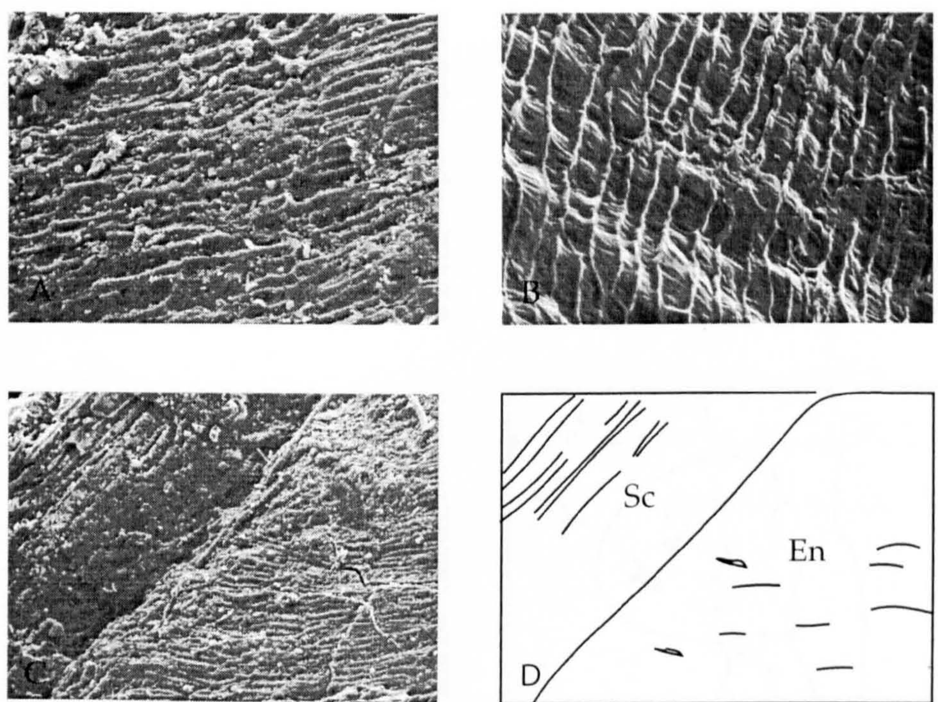


Figure 3. 9. Structures preserved in mineralised *Carex* sp. seeds from Potterne. A. Cell walls of endosperm tissue in mineralised *Carex* sp. seed (x 3800). B. Endosperm tissue of modern *Carex buxbaumii* seeds (x 4400). C. Mineralised *Carex* sp. seed showing endosperm tissue and mineralised rods representing casts of the sclerotic cells in the lower seed coat (x 1700). D. Schematic diagram of C (Sc = mineralised casts of sclerotic cells in lower seed coat. En = endosperm tissue showing preservation of cell walls).

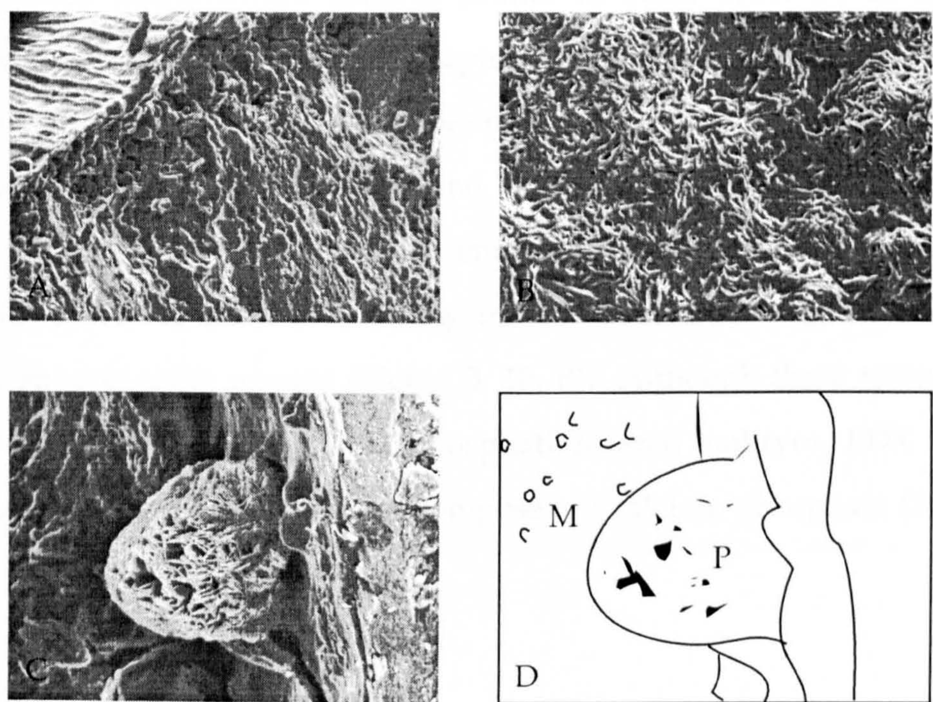


Figure 3.10. Textures preserved in minerlised *Carex* sp. seeds from Potterne. A. Modern *Carex buxbaumii* cotyledon interior (x 3800). B. Interior of Potterne *Carex* sp. seed showing a "porous" mineralised fabric (x 3800). C. Potterne *Carex* sp. seed cotyedon interior showing spherical porous mineralised structure and mineralised spheres in background (x 5000). D. Schematic diagram of C (M = mineralised spheres, making up bulk of cotyledons. P = mineralised structure with porous, platey fabric).

seed coat (Figure 3. 9. D). The cotyledons of the seed show some variation in preservational style. Two of the four specimens examined revealed phosphatised spheres similar to those observed in the other seed species (see above and Chapter 2). However, in addition to these, one specimen contained a number of sub-spherical structures, apparently made up of elongate plates or fine "whiskers" of mineral (Figure 3. 10. C & D). In another specimen, the entire cotyledon was apparently infilled with plates of mineral, resulting in very porous-looking structure, and no spheres were present (Figure 3. 10. B). Although these textures look very distinct from the other phosphatised seed embryos, EDX revealed that these cotyledons are also composed of calcium phosphate (Figures 3. 11. to 3. 13.).

3. 3. 2. 2. Seed coat structures

Although only *Urtica urens* among the Potterne fossil specimens retains its seed coat, the seed coat structure of modern specimens of all the seed taxa studied was investigated under SEM to establish if structure was a determining factor in the extent of mineralisation of different seeds. The coats of *Urtica urens* seeds are virtually featureless under SEM: in section, the 10 μm thick layer of collapsed cells shows no structure beyond lineations parallel to the surface (Figure 3. 14. A). In plan view from underneath, the basal seed coat layer comprises hexagonal cells with low relief cell walls (Figure 3. 8. C).

The seed coats of *Brassica nigra* (Figure 3. 14 C), *Hyoscyamus niger* (Figure 3. 14. E) and *Chenopodium album* (Figure 3. 15. A) are all similar in structure: the main structural layer comprises a palisade layer underlying an undulate epidermis, with an inner integument below it (Figures 3. 14. D & F and 3. 15. B). In the *Brassica* seed coat, the outer epidermal layer contains mucilaginous material (Cernohorsky, 1947).

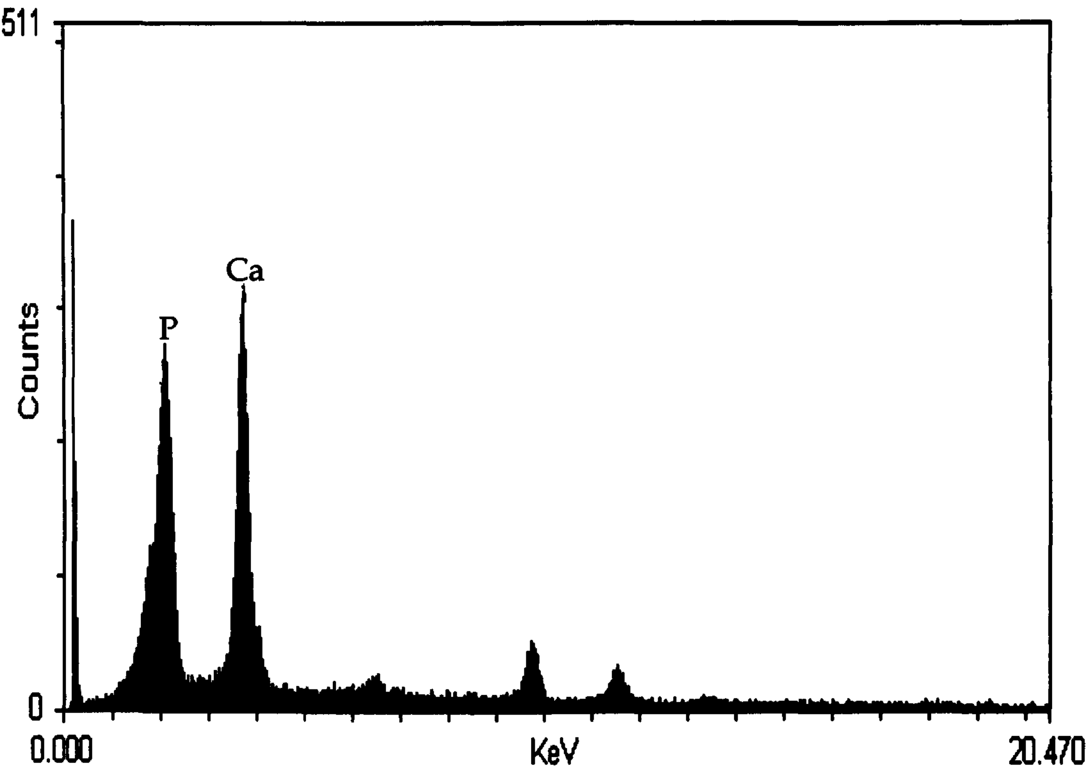


Figure 3. 11. EDX spectrum of a mineralised *Chenopodium* sp. seed from the Bronze age midden at Potterne, indicating a calcium phosphate mineralogy.

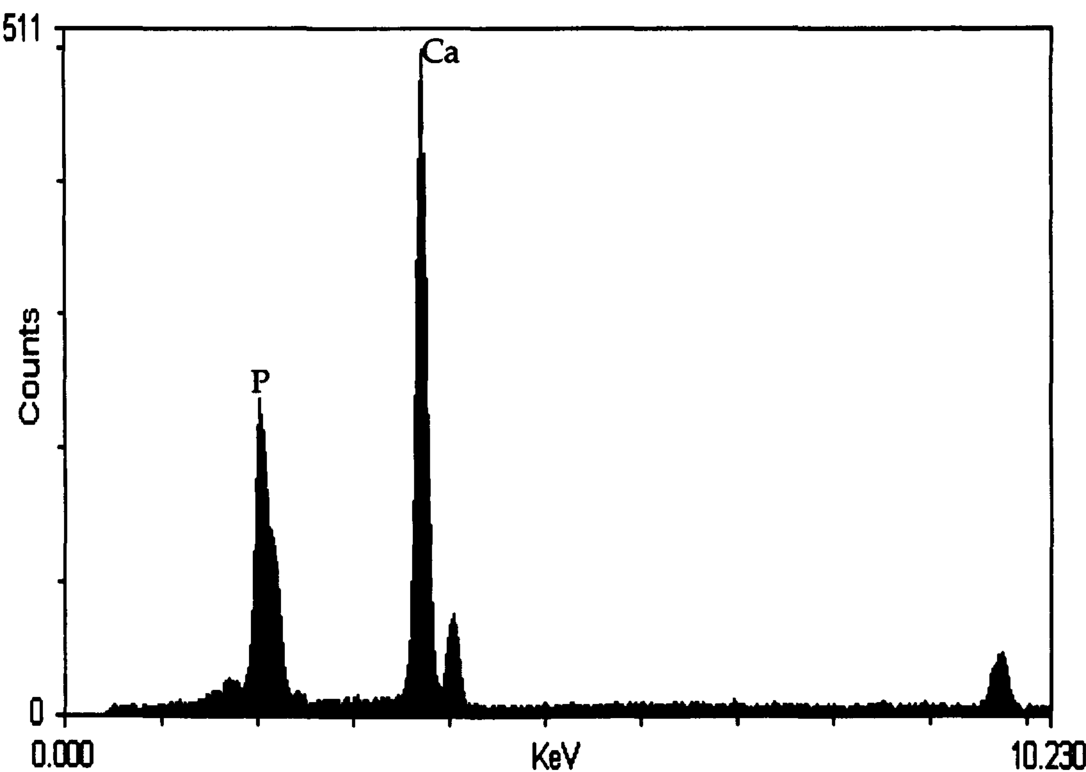


Figure 3. 12. EDX spectrum of a mineralised *Carex* sp. seed from the Bronze age midden at Potterne, showing a calcium phosphate mineralogy. The cotyledon area of this seed was structurally similar to that of other seed taxa preserved at the site.

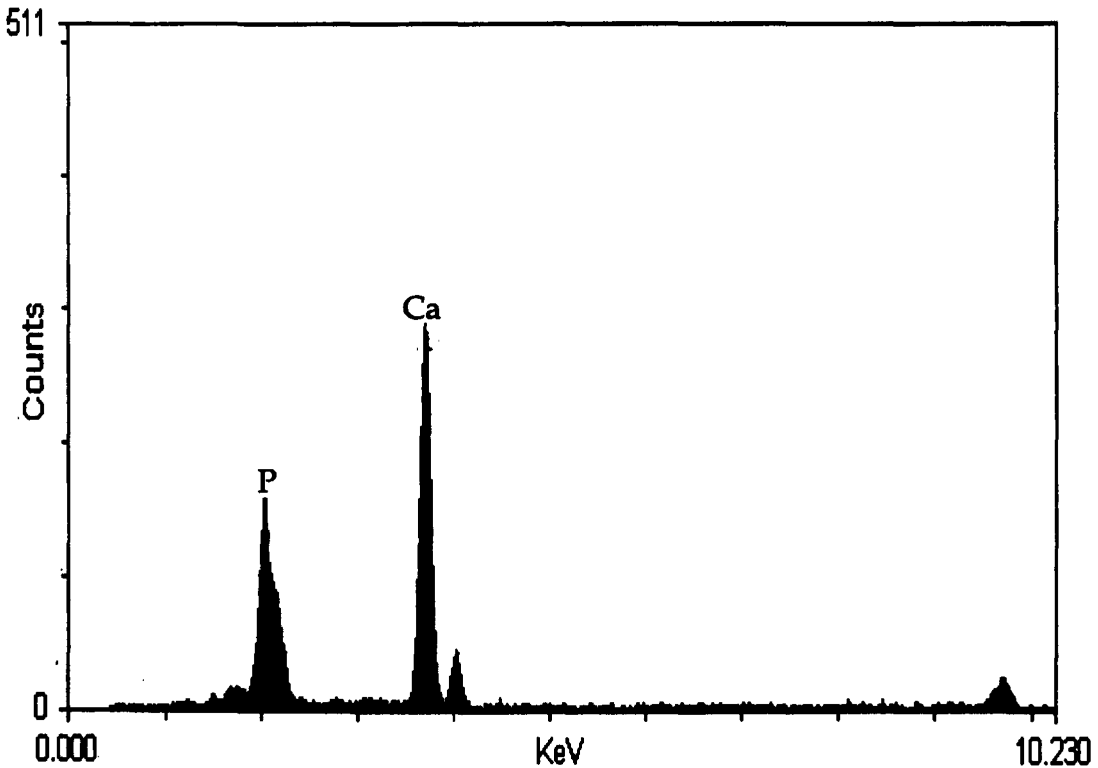


Figure 3. 13. EDX spectrum of a mineralised *Carex* sp. seed from the Bronze age midden at Potterne, showing a calcium phosphate mineralogy. The spectrum represents one of a number of sub-spherical structures with a porous texture which were observed in the cotyledon area of several *Carex* seeds.

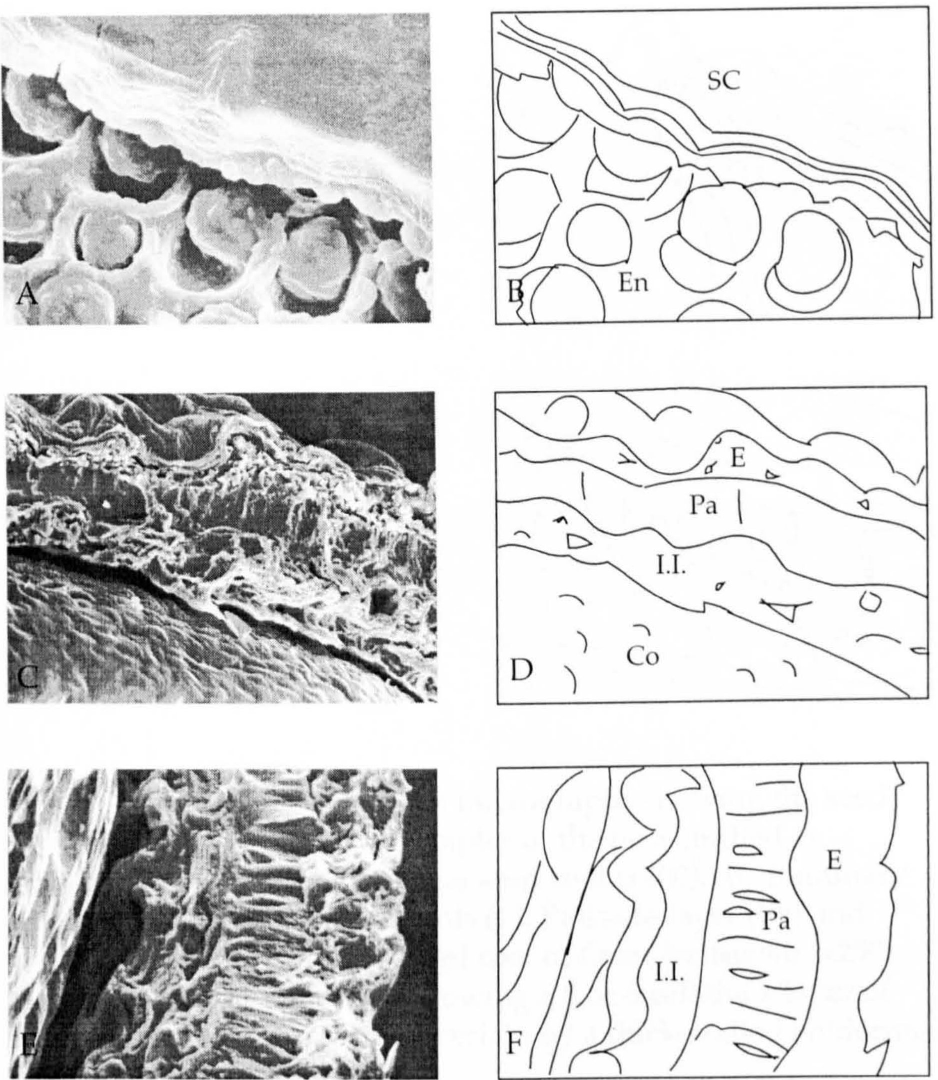


Figure 3. 14. Scanning electron micrographs showing the seed coat structures of modern examples of the taxa investigated at Potterne. A. *Urtica urens* seed coat and underlying endosperm tissue, showing lineations in the thin seed coat (x335). B. Summary diagram of A (En = endosperm; SC = seed coat). C. Seed coat and underlying cotyledon membrane of *Brassica nigra*(x 335). D. Summary diagram of C showing E (undulate epidermis), Pa (palisade layer), I. I. (inner integument) and Co (cotyledons). E. *Hyoscyamus niger* seed coat (x600). F. Summary diagram of E. showing palisade layer (Pa) with overlying epidermis (E) and underlying inner integument (I. I.).

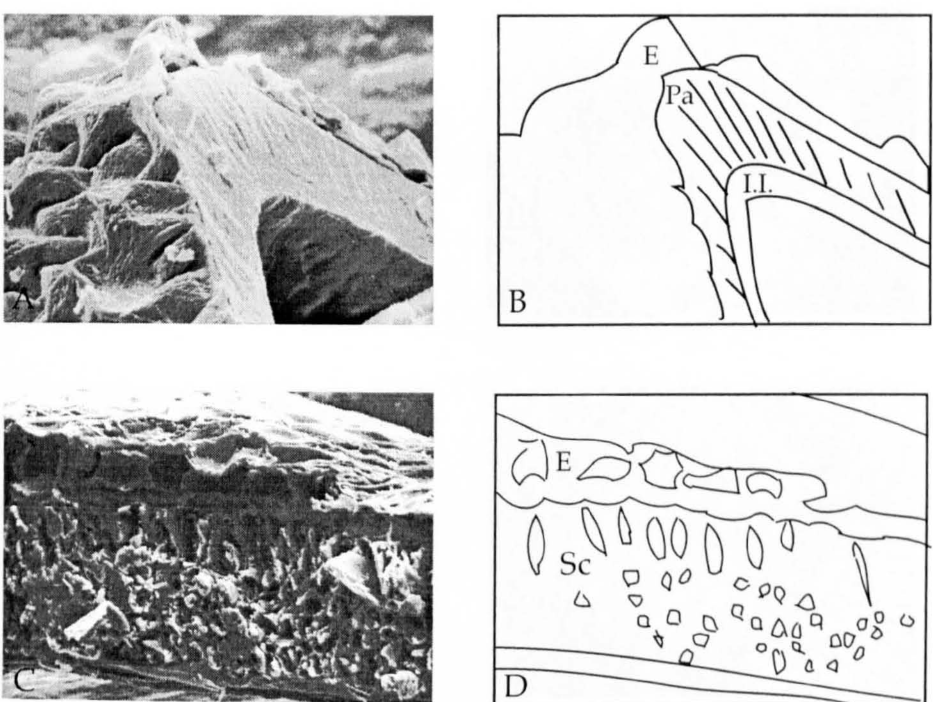


Figure 3. 15. Scanning electron micrographs showing the seed coat structures of modern examples of the taxa studied at Potterne. A. *Chenopodium album* seed coat (x400). B. Summary diagram of A showing epidermis (E), Palisade layer (Pa) and inner integument (I. I.). C. Seed coat of *Carex buxbaumii* (x250). D. Summary diagram of C. showing a 5 or 6 cell thick layer of schlerenchymous tissue (Sc) overlain by a thick-walled epidermis (E).

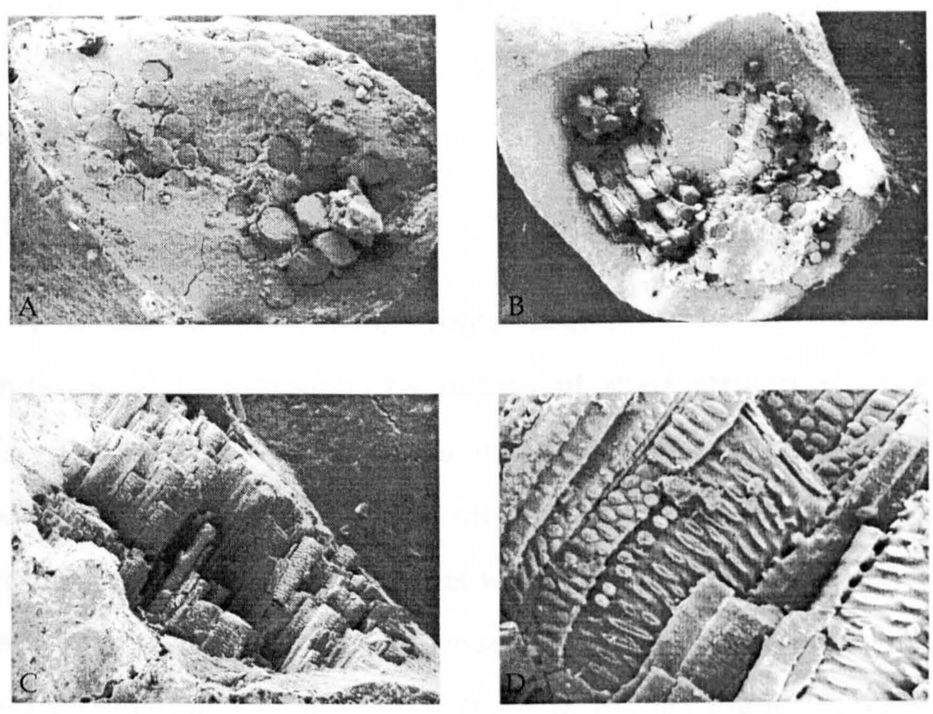


Figure 3.13 Structures preserved in mineralised roots from Potterne. A. View of end of mineralised Potterne root showing two main groups of vascular vessels (x 1000). B. View of a different mineralised Potterne root, again showing two distinct groups of vascular vessels (x 400). C. Close-up of end of Potterne mineralised root showing vascular vessels (x 600). D. Close-up of xylem vessels in mineralised Potterne root showing a pattern resulting from infilling of reticulate pits (x 3800).

The structure of the *Carex buxbaumii* seed coat (Figure 3. 15. B) is very distinct from the others, comprising an outer epidermal layer with thickened cell walls, underlain by a layer of schlerenchymous tissue, 5 or 6 cells thick, which is evident as long, hollow vessels in longitudinal section.

3. 3. 2. 3. Mineralised roots

A number of mineralised roots from Potterne were also examined under SEM to establish the nature of their structural preservation. Vascular vessels were obvious in all but one of the specimens (this exception revealed an apparently structureless cortex in transverse fractures). In the two specimens where the root end revealed very clear sections, the largest vascular vessels (typically the xylem vessels) form two distinct clusters (Figure 3. 16. A & B). At higher magnification, a pattern of relief is visible on the outer surface of individual xylem vessels (Figure 3. 16. C & D). This reflects the reticulate pattern of pits in the walls which decayed following infilling of the vessels (Figure 3. 17.). The large diameter of the xylem vessels relative to that of the root as a whole indicates that only the vascular cylinder is preserved. Thus, the outermost surface preserved is the endodermis rather than the epidermis.

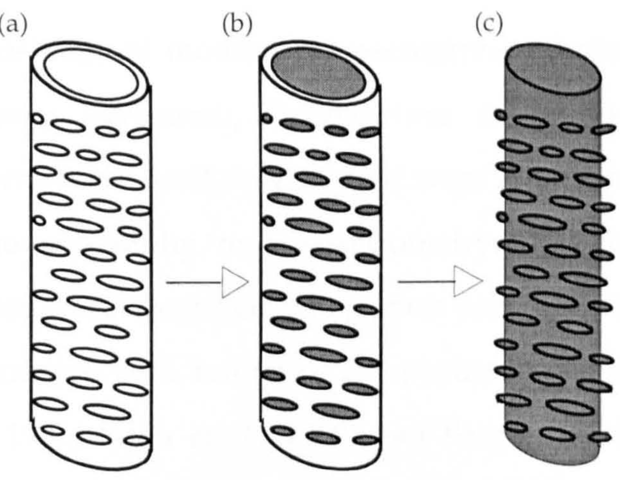


Figure 3. 17. Mode of phosphatisation of xylem vessels in Potterne roots. (a) A dead xylem vessel with a reticulate pattern of pits in its walls, (b) becomes infilled with calcium phosphate. Following decay of the organic xylem vessel walls, (c) an internal cast of the vessel's reticulate pits and central lumen remains.

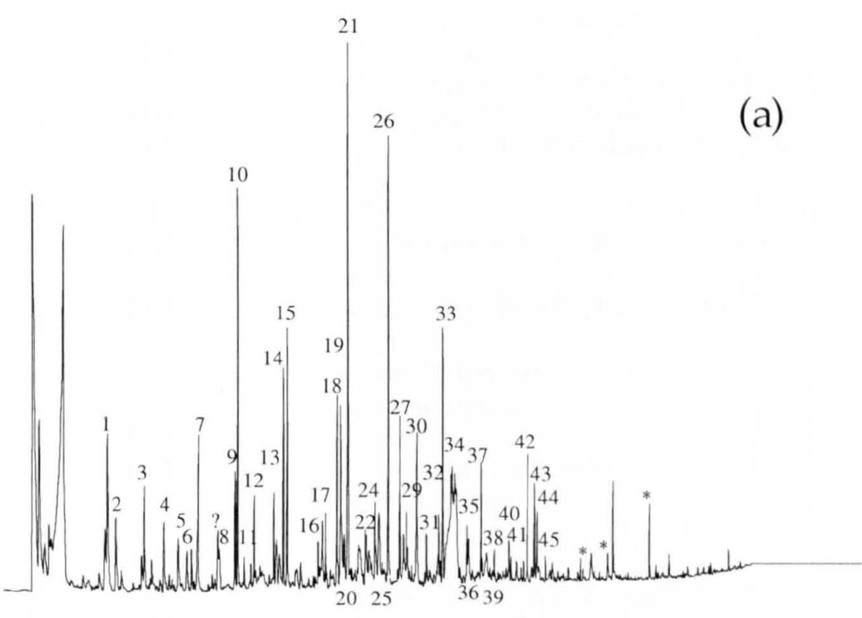
3. 3. 3. Composition of the seed coats

The chemical compositions of modern representatives (*Brassica nigra, Hyoscyamus niger, Carex buxbaumii, Chenopodium album* and *Urtica urens*) of the five Potterne fossil seed taxa studied were established using flash-pyrolysis gas chromatography/mass spectrometry. The compound peaks in the pyrolysates were identified using their retention times and mass spectral characteristics with reference to spectra in the literature (Ralph and Hatfield, 1991; Boon *et al.*, 1989; van Bergen *et al.*, 1997a; Pouwels *et al.*, 1989).

The pyrolysate of the *Carex buxbaumii* seed coat (Figure 3. 18. a; Table 3. 1.) is dominated by guaiacyl lignin products (guaiacol **(15)**, 4-vinylguaiacol **(26)** and *trans*-isoeugenol **(33)**) and phenols (phenol **(10)**, 4-methylphenol **(14)** and 4-vinylphenol **(21)**) typical of monocotyledons. Catechol **(19)** (1, 2-benzenediol), various polysaccharide moieties (e. g., 2, 3-dihydro-5-methylfuran-2-one **(7)**, 4-hydroxy-5, 6-dihydro-(2H)-pyran-2-one **(9)** and levoglucosan **(34)**) and syringyl lignin components (including syringol **(27)**, 2, 6-dimethoxy-4-vinylphenol **(32)** and trans-2, 6-dimethoxy-4-propenylphenol **(42)**) are also relatively abundant. This pyrolysate is very similar to that obtained for bromegrass (Ralph and Hatfield, 1991), with 4-vinylphenol and 4-vinylguaiacol present in strikingly high abundance relative to the other compounds. These dominant pyrolysis products arise from the major components in monocotyledon lignin, i.e. *p*-coumaric acid and ferulic acid (Boon *et al.*, 1989; Ralph & Hatfield, 1991; van Bergen *et al.*, 1994a).

The pyrolysate produced from the *Brassica nigra* seed coat (Figure 3. 18. b & Table 3. 2.) is dominated by the guaiacyl lignin products guaiacol **(15)** and 4-vinylguaiacol **(26)**, phenol **(9)** and 4-methylphenol**(14)**. Various polysaccharide moieties (including 1-acetoxypropan-2-one **(2)**, 2, 3-dihydro-5-methylfuran-2-one **(6)**, 1, 4-anhydroarabinofuranose **(19)** and

levoglucosan **(31)**) are also relatively abundant, along with other lignin derivatives (syringol **(27)**, vanillin **(29)**, trans-isoeugenol **(30)** and 2, 6-dimethoxy-4-vinylphenol **(33)**), catechol **(21)** and indole **(24)**. Typical dicotyledonous ligno-cellulose is dominated by syringyl products, and in some cases high relative abundances of guaiacyl products may also be present (van Bergen *et al.*, 1994a). However, phenol and 4-methylphenol are usually present in much smaller quantities in dicotyledons, as are catechol and indole. Although of ambiguous origin (they may be pyrolysis products of several groups of compounds, including lignins), the high relative abundances of the phenol and 4-methylphenol are not typical of lignin, suggesting that they may be derived at least partly from the amino acid tyrosine. The presence of indole (from tryptophan) and styrene (from phenylalanine) confirms that proteins *are* present in the seed coat. Catechols (1, 2-benzenediols) are also of uncertain origin; like phenols, these compounds are minor pyrolysis products of ligno-cellulose that are typically present in much smaller amounts. Non-hydrolysable tannin monomers (catechins) are known to yield 1, 2-benzenediols as major pyrolysis products (Galletti, 1991) but they may also be derived from cellulose (Pouwells *et al.*, 1989). Catechols in plant pyrolysates have been attributed to tannins by a number of authors (cone scales: Stankiewicz *et al*, 1997a; water lily fruit wall: van Bergen *et al.*, 1996; crab apple seed coats: McCobb *et al.*, in press). Although catechols were the dominant compounds in those pyrolysates and are much less significant here, they are still present in high enough relative abundances to make cellulose an unlikely source. Hence, the presence of tannins in the seed coat is likely. The *Brassica* seed coat pyrolysate does include a number of "typical lignin" derivatives, two of which (guaiacol and 4-vinylguaicol) are the most abundant products present. However, the higher than typical relative abundances of the other polyphenolic



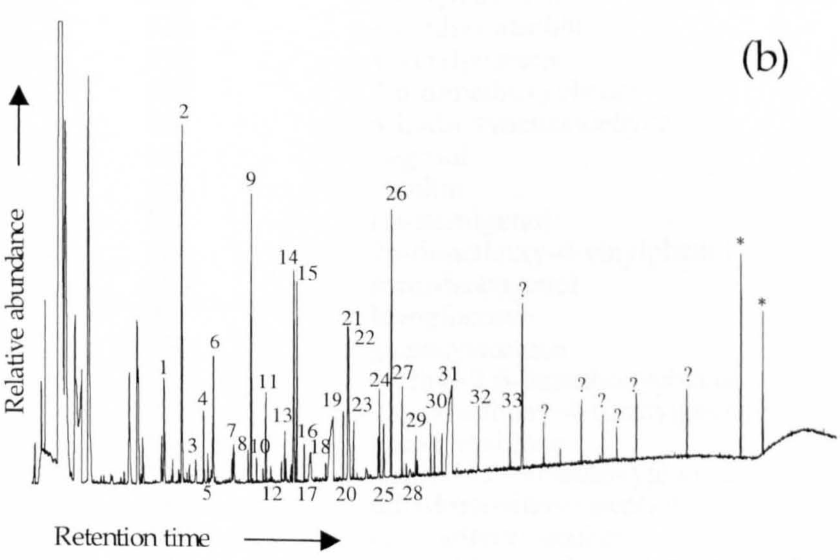


Figure 3. 18. Pyrograms (610°C/10 s) of modern seed coats. (a) *Carex buxbaumii*, (b) *Brassica nigra*. Peak numbers refer to compounds listed in Table 2.7. * = contaminants ? = unknown compounds.

Peak no:	M+·:	Compound name:	Origin:
1	96	furfural	PS
2	96	4-methyltetrahydrofuran-3-one	PS
3	98	2-hydroxymethylfuran	PS
4	84	(5H)-furan-2-one	PS
5	96	2-methyl-2-cyclopenten-1-one	PS
6	110	2-acetylfuran	PS
7	98	2,3-dihydro-5-methylfuran-2-one	PS
8	110	5-methyl-2-furaldehyde	PS
9	114	4-hydroxy-5,6-dihydro-(2H)-pyran-2-one	PS
10	94	phenol	?
11	112	3-hydroxy-2-methyl-2-cyclopenten-1-one	PS
12	112	2-hydroxy-3-methyl-2-cyclopenten-1-one	PS
13	108	2-methylphenol	?
14	108	4-methylphenol	?
15	124	guaiacol	L
16	122	2,4-dimethylphenol	?
17	122	4-ethylphenol	L
18	138	4-methylguaiacol	L
19	110	catechol	?
20	126	5-hydroxymethyl-2-furaldehyde	PS
21	120	4-vinylphenol	L
22	140	3-methoxycatechol	?
23	124	3-methylcatechol	L
24	152	4-ethylguaiacol	L
25	124	4-methylcatechol	L
26	150	4-vinylguaiacol	L
27	154	2,6-dimethoxyphenol	L
28	122	4-hydroxybenzaldehyde	L
29	164	eugenol	L
30	152	vanillin	L
31	164	*cis*-isoeugenol	L
32	180	26-dimethoxy-4-vinylphenol	L
33	164	*trans*-isoeugenol	L
34	98	levoglucosan	PS
35	180	guaiacylacetone	L
36	182	4-ethyl-2,6-dimethoxyphenol	L
37	180	2,6-dimethoxy-4-methylphenol	L
38	180	propiovanillone	L
39	194	4-allyl-2,6-dimethoxyphenol	L
40	182	dihydroconiferyl alcohol	L
41	180	*cis*-coniferyl alcohol	L
42	194	*trans*-2,6-dimethoxy-4-propenylphenol	L
43	178	*trans* coniferaldehyde	L
44	180	*trans* coniferyl alcohol	L
45	210	syringylacetone	L

Table 3. 1. Pyrolysis products detected in the seed coats of sedge (*Carex buxbaumii*) PS indicates a product derived from a polysaccharide, P indicates a product derived from a protein, L indicates a product derived from lignin, ? indicates a product of ambiguous origins. Products were identified based on their retention times and mass spectral characteristics with reference to published standards (Ralph & Hatfield, 1991; Stankiewicz *et al.*, 1998a; Pouwels *et al.*, 1987 & 1989).

Peak no:	M+•:	Compound:	Origin:
1	96	Furfural	PS
2	116	1-acetoxypropan-2-one	PS
3	84	(5H)-furan-2-one	PS
4	104	Styrene	P
5	110	2-acetylfuran	PS
6	98	2,3-dihydro-5-methylfuran-2-one	PS
7	110	5-methyl-2-furaldehyde	PS
8	114	4-hydroxy-56-dihydro-(2H)-pyran-2-one	PS
9	94	phenol	P?
10	98	2,4-dihydropyran-3-one	PS
11	112	2-hydroxy-3-methyl-2-cyclopenten-1-one	PS
12	110	2,3-dimethylcyclopenten-1-one	PS
13	108	2-methylphenol	?
14	108	4-methylphenol	?
15	124	guaiacol	L?
16	126	3-hydroxy-2-methyl-(4H)-pyran-4-one	PS
17	122	2,4-dimethylphenol	L
18	85	5-hydroxymethyl-2-tetrahydrofuraldehdye-3-one	PS
19	86	1,4-anhydroarabinofuranose	PS
20	138	cf. Ralf & Hatfield no. 50.	?
21	110	catechol	?
22	120	4-vinylphenol	L?
23	152	4-ethylguaiacol	L
24	117	indole	P
25	124	4-methylcatechol	L
26	150	4-vinylguaiacol	L
27	154	syringol	L
28	?	unknown hydrohexose	PS
29	152	vanillin	L
30	164	trans-isoeugenol	L
31	98	levoglucosan	PS
32	?	ß-ketan?	?
33	180	2,6-dimethoxy-4-vinylphenol	L

Table 3. 2. Pyrolysis products detected in the seed coats of the black mustard (*Brassica nigra*). PS indicates a product derived from a polysaccharide, P indicates a product derived from a protein, L indicates a product derived from lignin, ? indicates a product of ambiguous origins. Products were identified based on their retention times and mass spectral characteristics with reference to published standards (Ralph & Hatfield, 1991; Stankiewicz *et al.*, 1998a; Pouwels *et al.*, 1987 & 1989).

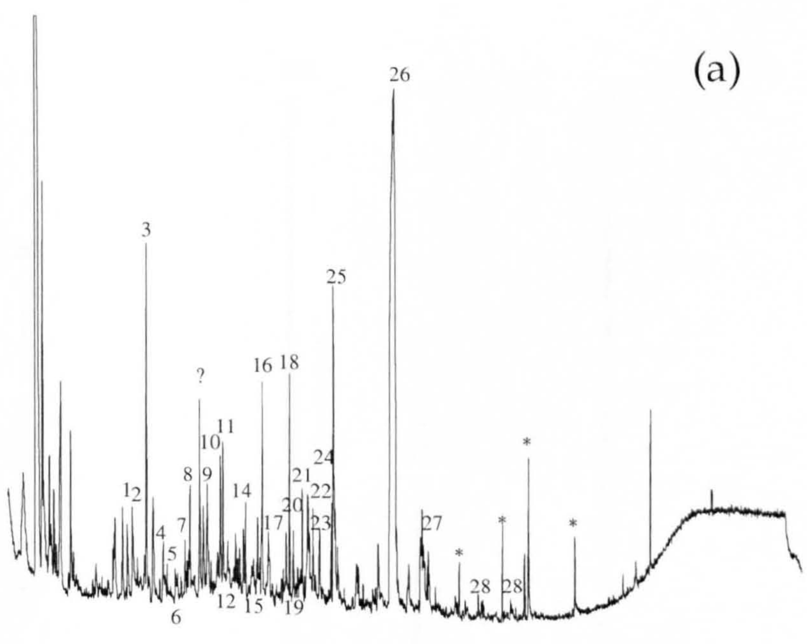
compounds suggest that proteins and tannins are present in addition to lignin and polysaccharides. The polysaccharide fraction of the pyrolysate includes some moieties associated with xylan (4-hydroxy-5, 6-dihydro-(2H)-pyran-2-one and 1, 4-anhydroarabinofuranose;), indicating the presence of this hemicellulose in addition to cellulose (Ohnishi *et al.*, 1977).

The majority of the products in the pyrolysate of a modern *Urtica urens* seed coat (Figure 3. 19. A & Table 3. 3.) are polysaccharide markers, derived from cellulose and hemicelluloses. The most abundant compound is levoglucosan **(27)**, although a number of other products are also relatively abundant (furfural **(3)**, 5-hydroxymethyl-2-tetrahydrofuraldehyde-3-one **(18)** and 1, 4-dideoxy-D-glycerohex-1-enopyranos-3-ulose **(25)**. In addition to the polysaccharide markers, some less diagnostic compounds are present, including phenol **(11)**, methylphenols **(15)** and benzoic acid **(19)**. These compounds may potentially be derived from pyrolysis of lignins (Ralph & Hatfield, 1991) but the absence of diagnostic lignin markers such as guaiacols and syringols from the pyrolysate makes this an unlikely source. Phenol and methylphenols are also pyrolysis products of the amino acid tyrosine (Tsuge & Matsubara. 1985), and the presence of proteins in the seed coat is confirmed by the detection of 2,5-Diketopiperazine derivatives **(28)**, diagnostic compounds generated by pyrolysis of dipeptides (Stankiewicz *et al.*, 1996). Although the majority of the polysaccharide moieties detected may be produced by pyrolysis of cellulose (Pouwels *et al*, 1989; Ralph & Hatfield, 1991), the presence of one or more hemicelluloses is also likely. The compound 1,4-anhydroxylofuranose is a pyrolysis marker for xylan (Ralph & Hatfield, 1991), and an unknown polysaccharide product in the *Urtica urens* seed coat pyrolysate has a mass spectrum and retention time consistent with a compound

produced by pyrolysis of xylan (Pouwels *et al.*, 1987: Table 1, compound no. 127). The small nettle seed coat pyrolysate has a strikingly high proportion of polysaccharide pyrolysis markers, suggesting that the composition is dominated by these carbohydrates, with relatively minor amounts of proteins present. There are no compounds in the nettle seed coat pyrolysate to suggest the presence of lignins.

To establish the nature of the polysaccharide component of the *Urtica urens* seed coats, acid hydrolysis and derivatisation were used to separate the monosaccharides that make up the carbohydrate fraction of the seed coats. The resulting sugars were then separated using gas chromatography and identified based on their retention times. The GC trace (Figure 3. 20.) shows that five sugars are present in the nettle seed coats: arabinose, xylose, mannose, galactose and glucose. The presence of glucose as the most abundant sugar in the seed coats is unsurprising, as this is the building block of cellulose, the major polysaccharide present. However, apart from its role as the sole building block of cellulose, glucose may be found as a component of various hemicelluloses, along with other monosaccharides. For example, xylans principally comprise a chain of (1>4)-linked ß-D-xylose units but also commonly contain other sugars, such as arabinose and glucose, as side chains. Similarly, while some mannans contain just (1>4)-linked ß-D-mannose units, others also have ß-D-glucose in their main backbone structure and they may have other sugars (e. g. galactose) as side chains. Galactose is also the main building block of the galactans, a third group of hemicelluloses, which may also have additional sugars as side chains. Hence, the monosaccharides detected indicate that two or more hemicelluloses are present in the seed coats, in addition to cellulose.

The pyrogram (Figures 3. 19. B & Table 3. 4.) of a *Hyoscyamus niger* seed coat is dominated by various polyphenolic compounds (phenol (7),



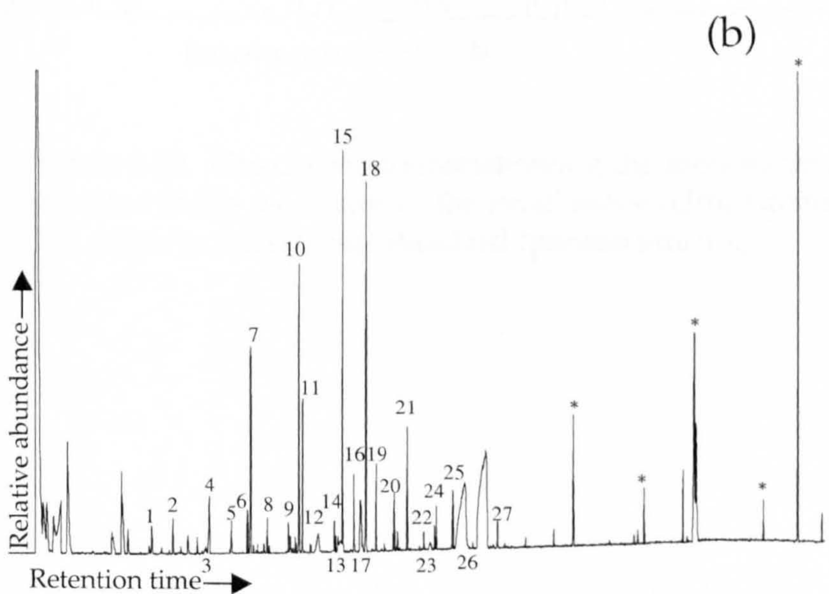


Figure 3. 19. Pyrograms of modern seed coats.
(a) *Urtica urens* and (b) *Hyoscyamus niger.*
* = contaminants (pthalates)

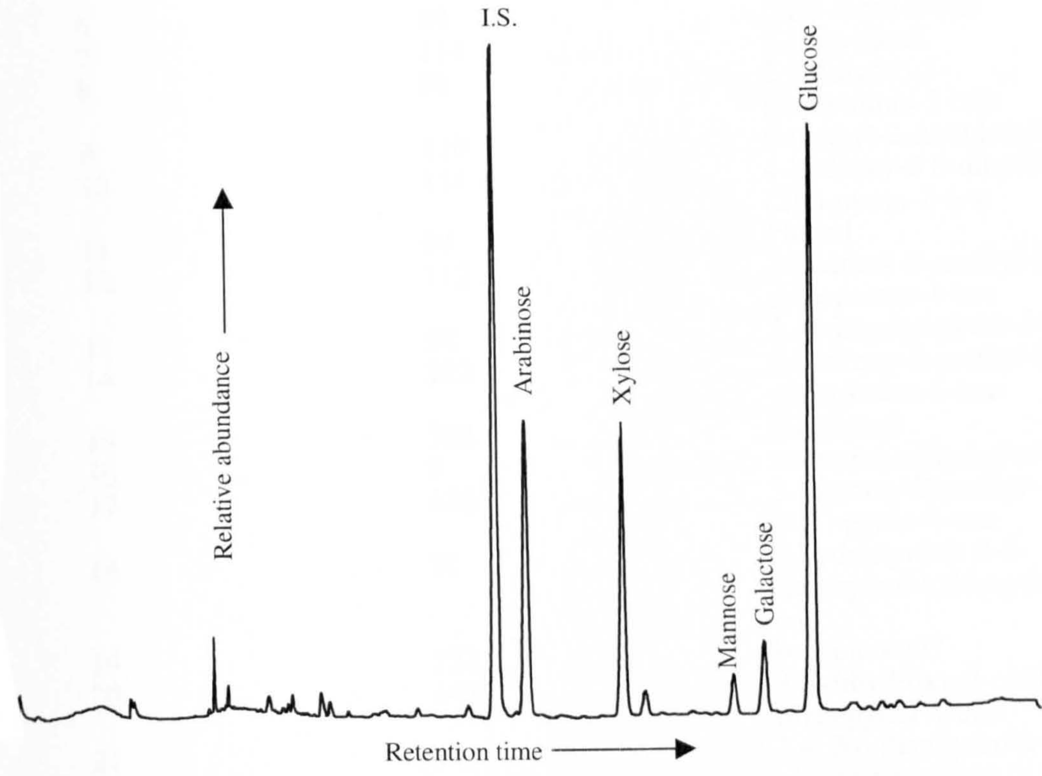


Figure 3.20. Gas chromatogramshowing the monosaccharides detected in the seed coats of the small nettle (*Urtica urens*). I. S. refers to the internal standard (pentaerythritol).

Peak number:	M+.:	Compound:	Origin:
1	84	(2H)-furan-3-one	PS
2	96	3-furaldehyde	PS
3	96	furfural	PS
4	98	2-hydroxymethylfuran	PS
5	96	cyclopent-1-ene-3 4-dione	PS
6	84	(5H)-furan-2-one	PS
7	110	2-acetylfuran	PS
8	98	2 3-dihydro-5-methylfuran-2-one	PS
9	110	5-methyl-2-furaldehyde	PS
10	114	4-hydroxy-5 6-dihydro-(2H)-pyran-2-one	PS
11	94	Phenol	PS/P
12	112	2-hydroxy-3-methyl-2-cyclopenten-1-one	PS
13	98	2, 4-dihydro-pyran-3-one	PS
14	112	3-hydroxy-2-methyl-2-cyclopenten-1-one	PS
15	108	C1-phenol	P
16	?	unknown anhydrohexose	PS
17	126	3-hydroxy-2-methyl-(4H)-pyran-4-one	PS
18	85	5-hydroxymethyl-2-tetrahydrofuraldehyde-3-one	PS
19	122	benzoic acid?	?
20	142	3 5-dihydroxy-2-methyl-(4H)-pyran-4-one	PS
21	144	1 4: 3 6-dianhydro-a-D-glucopyranose	PS
22	126	5-hydroxymethyl-2-furaldehyde	PS
23	113	C1-pyrrolidinedione	P
24	86	1 4-anhydroxylofuranose	PS
25	144	1 4-Dideoxy-D-glycerohex-1-enopyranos-3-ulose	PS
26	98	Levoglucosan	PS
27	115	1 6-anhydro-ß-D-glucofuranose	PS
28	168	2 5-diketopiperazine derivatives	P

Table 3. 3. Pyrolysis products detected in the seed coats of the small nettle (*Urtica urens*). PS indicates a product derived from a polysaccharide, P indicates a product derived from a protein. Products were identified based on their retention times and mass spectral characteristics with reference to published standards (Ralph & Hatfield, 1991; Stankiewicz *et al.*, 1998; Pouwels *et al.*, 1987 & 1989).

Peak no:	M+•:	Compound name:	Origin:
1	96	furfural	PS
2	98	2-hydroxymethylfuran	PS
3	110	2-acetylfuran	PS
4	98	2,3-dihydro-5-methylfuran-2-one	PS
5	110	5-methyl-2-furaldehyde	PS
6	114	4-hydroxy-5,6-dihydro-(2H)-pyran-2-one	PS
7	94	phenol	?
8	112	2-hydroxy-3-methyl-2-cyclopenten-1-one	PS
9	108	2-methylphenol	?
10	108	4-methylphenol	?
11	124	guaiacol	L
12	126	3-hydroxy-2-methyl-(4H)-pyran-4-one	PS
13	122	2,6-dimethylphenol	L
14	85	5-hydroxymethyl-2-tetrahydrofuraldehyde-3-one	PS
15	122	2,4-dimethylphenol	L
16	138	4-methylguaiacol	L
17	110	catechol	?
18	120	4-vinylphenol	P?
19	136	4-ethyl-2-methylphenol	L
20	117	indole	P
21	150	4-vinylguaiacol	L
22	154	syringol	L
23	131	skatole (3-methylindole)	P
24	152	vanillin	L
25	168	2,6-dimethoxy-4-methylphenol	L
26	98	levoglucosan	PS
27	180	2,6-dimethoxy-4-vinylphenol	L

Table 3. 4. Pyrolysis products detected in the seed coats of henbane (*Hyoscyamus niger*). PS indicates a product derived from a polysaccharide, P indicates a product derived from a protein, L indicates a product derived from lignin, ? indicates a product of ambiguous origins. Products were identified based on their retention times and mass spectral characteristics with reference to published standards (Ralph & Hatfield, 1991; Stankiewicz *et al.*, 1998a; Pouwels *et al.*, 1987 & 1989).

4-methylphenol **(10)**, 2, 4-dimethylphenol **(15)** and 4-vinylphenol **(18)**). Other significant peaks represent lignin derivatives (guaiacol **(11)**, 4-methylguaiacol **(16)**, 4-vinylguaiacol **(21)** and vanillin **(24)** and protein products (indole **(20)** and 3-methylindole **(23)**). With the exception of levoglucosan, polysaccharide moieties (e. g. furfural **(1)**, 2, 3-dihydro-5-methylfuran-2-one **(4)** and 4-hydroxy-5, 6-dihydro-(2H)-pyran-2-one **(6)**) are present at comparatively low relative abundances. 4-vinylphenol **(18)** is typically very plentiful in monocotyledonous angiosperm lignin, as a pyrolysis product of *p*-coumaric acid, but it is usually a relatively minor component of dicotyledons such as *Hyoscyamus niger* (e. g., see van Bergen *et al.*, 1994a). Similarly, 2, 4-dimethylphenol **(15)** is usually present as a minor lignin product in dicotyledonous seeds. Lignin structure is known to vary greatly between taxa and even within different parts of an individual plant (van Bergen *et al.*, 1994a & Boon *et al.*, 1989), so one explanation for this unusual pyrolysate may be a highly unconventional lignin composition. However, vinylphenol and 4-methylphenol may both be derived from the amino acid tyrosine (Stankiewicz *et al.*, 1997b; Chiavari & Galletti, 1992), and the presence of proteins is confirmed by the indole **(20)** and skatole **(23)** (3-methylindole) peaks (both indicative of the amino acid tryptophan; Chiavari & Galletti, 1992). This suggests that proteins may form a significant part of the seed coat, along with the more usual lignin and cellulose components.

The pyrogram (Figure 3. 21. & Table 3. 5.) yielded by the *Chenopodium album* seed coat is also very different from typical ligno-cellulose traces. Although polysaccharide compounds are relatively abundant, typical lignin products are relatively rare, and other, less specific, polyphenolic compounds dominate (phenol **(5)**, catechol **(11)** (1, 2-benzenediol) and methylcatechols **(13, 15, 17)**). The dominant polysaccharide peaks include furfural **(1)**, 2, 3-dihydro-5-methylfuran-2-one **(3)**, 5-methyl-2-

furaldehyde (**4**), levoglucosan (**18**) and 1, 4-arabinofuranose (**9**), indicating the presence of both cellulose and one of the arabinoxylans (a hemicellulose). Although lignin chemistry is known to vary significantly (van Bergen *et al.*, 1994a; Boon *et al.*, 1989), with different relative contributions from guaiacol and syringol units, the only "lignin" markers detected in the *Chenopodium* seed coat are guaiacol (**8**) and 4-vinylguaiacol (**16**) and these make only a minor contribution to the pyrolysate, suggesting that lignins are absent or very minor. The source of the polyphenolic compounds that dominate this pyrolysate is not certain. Although phenols and 1, 2-benzenediols (catechols) have been recognised previously in lignified tissues, they are usually present in much lower relative abundances, with guaiacyl (2-methoxyphenol) and syringyl (2, 6-dimethoxyphenol) compounds dominant. They may be derived from minor lignin components in the *Chenopodium* seed coat.

It is likely that a non-lignin macromolecule dominates the polyphenolic fraction in the *Chenopodium* seed coat. Non-hydrolysable tannin monomers (catechins) yield abundant 1, 2-benzenediols on pyrolysis (Galletti, 1991), and these compounds have been suggested as the source of catechol derivatives in the pyrolysates of modern conifer cone scales (Stankiewicz *et al.*, 1997a), of the fruit wall of the water lily *Nelumbo* (van Bergen *et al.*, 1997a), and of crab apple seed coats (Chapter 2; McCobb *et al.*, in press). It has even been suggested that pyrolysis of tannins may yield "guaiacyl" compounds such as those in the *Chenopodium* pyrolysate, based on the substitution of the B-ring in the catechin (van Bergen, *pers comm.*, 1999). In addition to tannins, the presence of proteins in the *Chenopodium* seed coat is indicated by the presence of styrene (derived from the amino acid phenylalanine) and indole (derived from tryptophan). Phenol and 4-methylphenol, two of

PAGE NUMBERING AS ORIGINAL

Peak no:	M+·:	Compound name:	Origin:
1	96	furfural	PS
2	104	styrene	P
3	98	2,3-dihydro-5-methylfuran-2-one	PS
4	110	5-methyl-2-furaldehyde	PS
5	94	phenol	P?
6	108	2-methylphenol	P?
7	108	4-methylphenol	P?
8	124	guaiacol	L?
9	86	1,4-arabinofuranose?	PS
10	122	4-ethylphenol	L
11	110	catechol	?
12	120	4-vinylphenol	L/P?
13	124	3-methylcatechol	L
14	117	indole	P
15	124	methylcatechol	L
16	150	4-vinylguaiacol	L
17	?	methylcatechol?	L
18	98	levoglucosan	PS

Table 3. 5. Pyrolysis products detected in the seed coats of fat hen (*Chenopodium album*). PS indicates a product derived from a polysaccharide, P indicates a product derived from a protein, L indicates a product derived from lignin, ? indicates a product of ambiguous origins. Products were identified based on their retention times and mass spectral characteristics with reference to published standards (Ralph & Hatfield, 1991; Stankiewicz *et al.*, 1998a; Pouwels *et al.*, 1987 & 1989).

the dominant peaks in the pyrolysate, may also be derived from the amino acid tyrosine, although phenol is a common pyrolysis product with many potential sources. It is likely that *Chenopodium* seed coats have an unusual composition, comprising a protein-tannin-polysaccharide complex similar to the non-cellulose polysaccharide/tannin composition proposed for *Nelumbo* fruit walls (van Bergen *et al.*, 1997a). A similar composition was proposed for *Agrostemma githago* seed coats (Chapter 2) and the *Hyoscyamus niger* seed coats discussed above, although phenols were more prevalent in both cases, suggesting a greater contribution from proteins.

3. 4. Discussion

3. 4. 1. General model for the phosphatisation of the seeds and roots in the Potterne midden

The midden at Potterne was characterised by periods of significant deposition of organic-rich material, alternating with periods of less deposition, during which opportunistic plants could move in and colonise it (Figure 3. 22.). Based on the composition of the fossil seed assemblage, the majority of these weeds were annuals, although a few perennials were present. It is not clear whether the latter persisted from year to year or re-colonised regularly along with the annual plants. Once significant deposition of organic waste resumed, the plants growing on the midden were smothered and their vegetative parts decayed, although their seeds (and some roots; see **3. 4. 3.** for detailed explanation) persisted in the midden soil. Decay of the abundant organic matter present in the midden eventually turned this newly buried soil level anoxic and mildly acidic, creating the conditions needed for phosphatisation. Concentrations of pore water phosphate and calcium ions were high at this stage, due to the degradation of the numerous

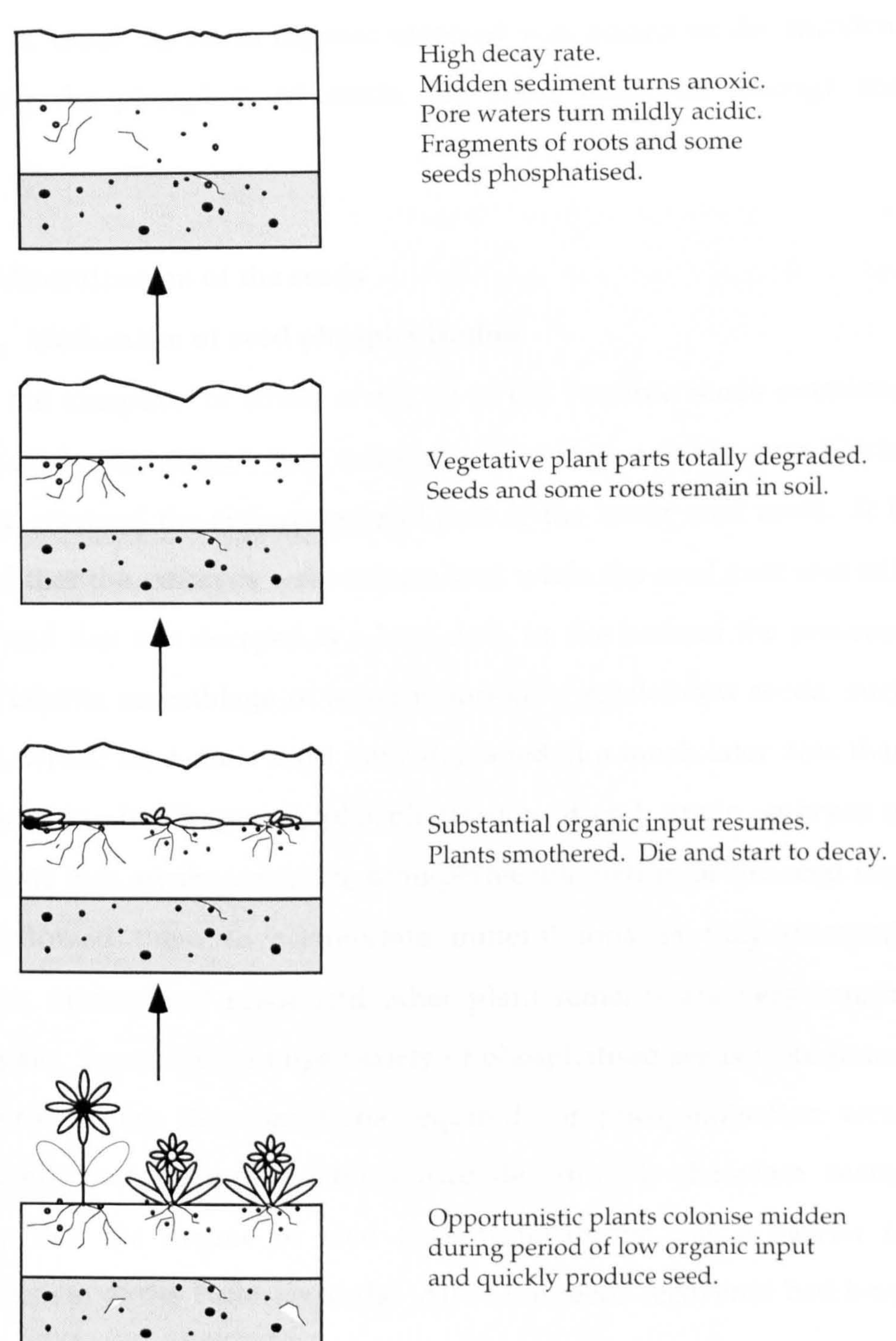


Figure 3. 22. Diagrams summarising the likely cycle of events that led to the formation of phosphatised seeds and roots inthe Potterne midden. This cycle was repeated throughout the durationof midden use, creating phosphatised plant remains at all levels of the midden. The shaded layer represents an horizon of the midden sediment in which plant roots can no longer survive but which favours phosphatisation.

organic remains added to the midden, allowing replacement of the decaying seed and root tissues by calcium phosphate. Hence, some of the seed bank and roots were phosphatised. This cycle was repeated a number of times, as more organic material was added to the midden, producing the phosphatised seeds and roots observed through the deposit.

3. 4. 2. Mineralisation of the seeds

3. 4. 2. 1. Mechanism of seed phosphatisation

With the exception of *Urtica urens*, all of the Potterne seeds examined in this study comprised just mineralised embryos (only one *Carex* specimen retained the endosperm and part of the lower seed coat). It is assumed that the embryos were mineralised while the seed coat was still present and that this decayed at a later date, on the basis of the presence in the Potterne assemblage of some notoriously recalcitrant seeds, such as elder, whose seed coats must have degraded at a much later date than their embryos. In **Chapter 2**, phosphatisation of crab apple embryos at Coppergate was attributed to the semi-permeable nature of the seed coat which allowed them to accumulate mineral ions as they decayed. However, mineralised seeds and other plant remains are very rare at Coppergate. In contrast, a huge variety of phosphatised seeds were found at Potterne where the conditions required for phosphatisation were presumably met throughout the entire deposit. It therefore seems unlikely that the degree of seed coat permeability was a barrier to mineralisation of the Potterne seeds. All of the seeds recovered had been phosphatised in an imbibed state, i.e. the seed had taken up water and swollen, a process which normally precedes germination. As already mentioned, some seeds possess a semi-permeable membrane beneath the seed coat, which allows water in and which controls the entry of

solutes, only letting through those below a certain size. However, once a seed dies the membrane can no longer exclude solutes and these can "leak" in or out. Hence, it is possible that the Potterne fossil seeds represent dead seeds in which any semi-permeable membrane controlling the movement of ions and bacteria no longer functioned, allowing decay and phosphatisation of the embryos to take place. Any seeds lacking semi-permeable membranes would require only some damage to the seed coat to allow microbial and ionic access to the embryo.

3. 4. 2. 2. The influence of structure versus chemical composition in determining the extent of seed phosphatisation

One of the main aims of this study was to establish whether structural or compositional factors were responsible for the variation in the extent of seed phosphatisation in specimens recovered from the Potterne midden. Analysis by py-GC/MS of the five plant taxa shows that seed coat composition varies enormously. Although a ligno-cellulose complex is thought to be "the norm" for angiosperm seed coats, no two of the species studied have the same composition. Only *Carex buxbaumii* has a "typical" seed coat composition, that of monocots, the angiosperm group to which it belongs. Among the dicots, none of the seed coats is exclusively lignified, as is considered usual for angiosperms. *Brassica nigra* and *Hyoscyamus niger* both appear to have significant amounts of proteins present with lignin, and also tannins. *Chenopodium album* seed coats appear to comprise non-hydrolysable tannins, and may lack lignin altogether. The small nettle (*Urtica urens*) seed coats have a composition apparently dominated by polysaccharides (both cellulose and hemicelluloses), with a less significant protein component and no evidence for the presence of lignins at all.

This great variety of compositions suggests that the chemistry of a particular seed coat did not dictate whether or not it was phosphatised in the Potterne midden. If this were the case, it would be predicted that the seeds would show a variety of preservational styles, whereas only *Urtica urens* and one or two other species retain the seed coat in the Potterne fossils. However, the apparent total absence of lignins from the nettle seed coats is unusual, and is likely to have a significant impact on preservation potential, as polysaccharides are known to be much less decay-resistant than lignins (Hedges *et al.*, 1985). If this were the case, it would seem counterintuitive that nettle seeds should be among the most common seeds recovered from the archaeological deposits in general (see **Chapter 4**). Although their presence in many archaeological deposits can be explained by their role as opportunistic, prolific and highly successful weeds, the unusual composition of their seed coats might be expected to taphonomically exclude them from significantly degraded deposits, in favour of seeds with more "conventional" ligno-cellulose coats.

However, given the deviation from a ligno-cellulose composition of the majority of the seed coats studied in this thesis, it is possible that under lower decay rates than are required for phosphatisation, the *Urtica urens* seed coats may survive for relatively long periods of time. On the basis of the persistence of polysaccharides (both hemicelluloses and cellulose) in the cess pit seed coats analysed in **Chapter 2**, it appears that these biomolecules degrade slowly and gradually over many years under relatively waterlogged conditions.

In terms of structure, the coats of *Urtica urens* seeds are very thin (~ 10μm), with thin cell walls, and they do not differentiate into a distinct layers as do the majority of seed coats. The collapsed nature of the cells made it very difficult to distinguish any detail in either modern or fossil

specimens beyond vague lineations under SEM (Figure 3. 14 A). The structure of the seed coat is more complex in the other seeds studied, with each species typically possessing a coat made up of several layers of different cell types (Figures 3. 14. & 3. 15.). The thin, uncomplex seed coat of the nettle, made up of collapsed relatively uniform, thin-walled cells is likely to be much more susceptible to microbial attack than thick coats which comprise a number of different cell types, some of which possess thickened cell walls.

It is likely that the susceptibility of *Urtica urens* seed coats to phosphatisation can be attributed to a combination of their very thin, undifferentiated structure and their lack of lignin. Indeed, the structural and compositional characteristics of the coats are presumably linked, as a thick, complex seed coat is more likely to require the presence of lignins or tannins to strengthen cell walls. However, although a thick, complex seed coat could not decay as rapidly as a thin, simple one, the unusual chemical composition of the coats is likely to have had the most impact on its preservation potential. A lack of lignins, tannins and a significant protein content would allow the polysaccharide-rich seed coats to degrade very rapidly, facilitating their replacement by calcium phosphate. The coats of the other seed taxa presumably degraded too slowly to allow their phosphatisation to take place. Since these taxa represent a range of both seed coat structures and compositions, their intrinsic decay resistance is likely to result from a combination of both these.

3. 4. 3. Mineralisation of the Potterne roots

During her original study of the Potterne mineralised plant material, Carruthers (2000) sent a number of mineralised roots to T. Lawrence at the Jodrell Laboratory, Kew Gardens, for identification. Although precise

taxonomic identification was not possible, the roots were all declared to be dicotyledonous and very similar to each other, suggesting that they all belonged to closely related, if not the same, species. These observations were borne out by examination of root fragments under SEM for this study. Examination of the root specimens in which clear sections of the internal structure are visible indicated that the roots belong to dicotyledonous plants (based on the fact that within the vascular cylinder, the xylem vessels are grouped into a small number of bundles, rather than scattered throughout the root matrix as in monocotyledons), and they display a diarch distribution of the vascular tissue (i.e., there are two distinct bundles of xylem vessels).

3. 4. 3. 1. Mineralisation of the central stele

The large proportions of vascular vessels in the mineralised roots indicate that they represent only the central vascular cylinder or stele, rather than the entire root structure. There are two possible explanations for this. Firstly, the vascular cylinder may have been selectively mineralised, while the surrounding cortex of the root decayed. In this scenario, the vascular vessels were preferentially mineralised because they conduct the ion-laden pore waters necessary for phosphatisation. The mineral-infilled vessels acted as a nucleus for phosphatisation, and the surrounding matrix tissue of the central stele was also mineralised. This process failed to phosphatise the entire root, however, perhaps because decay was too rapid, or because insufficient ions remained.

Selective mineralisation of the stele seems unlikely as the cortex of the root is comprised of the same parenchymous cells as the pith of the vascular cylinder, and should therefore decay at a similar rate. Furthermore, the exodermis of active root tips and some epidermal cells

of young roots are covered with a mucilaginous, polysaccharide film, designed to facilitate smooth movement of the roots through the soil. This film also promotes high levels of microbial activity in the soil immediately surrounding the roots, to facilitate the release of nutrient ions in a form which the roots can absorb. Therefore, on death, the outer surface of a root would seem to be a prime location for phosphatisation; masses of bacteria would already be present, capable of decaying the root at a fast enough rate to make its fossilisation a realistic possibility if the other conditions required for mineralisation were met. The absence of sufficient ions to phosphatise the root beyond the vascular cylinder could be a limiting factor, but mineralisation of at least some entire fine roots would be expected, and yet none has been recovered. It is possible that these were present but were so fragile that they became broken up during sediment processing.

An alternative explanation for phosphatisation of the vascular cylinder of the roots is that this was the only part of the root present when mineralisation was initiated. The central stele of roots is often the only part remaining, particularly among mature or perennial plants, in which the root cortex decays on maturity, making the endodermis the functional outer surface.

3. 4. 3. 2. Selective mineralisation of dicotyledonous roots versus monocotyledonous roots at Potterne

The discussion above explains how the Potterne roots are likely to have been phosphatised but it does not address the reasons for the apparent taxonomic bias towards dicotyledonous roots. Two factors may have contributed to this bias: anatomical differences and life cycle differences.

3. 4. 3. 2. 1. Anatomical differences

In addition to the distinct arrangement of vascular vessels, the root anatomy of monocot and dicot roots differs in a number of ways. Mature dicotyledonous plants typically have a tap root from which a number of smaller branches arise, whereas monocotyledons have adventitious roots that develop from the stem (Fahn, 1982). This in itself is unlikely to create any taphonomic differences between the two groups. Potentially more significant is the fact that the mature roots of dicots become tough and robust through secondary thickening, whereas the adventitious roots of monocots typically remain unstrengthened. Few plants could thrive under the sediment conditions required for phosphatisation (anaerobic, partially waterlogged with acidic pore waters and very high microbial activity; see Chapter 2), so it is assumed that those living on the Potterne midden died long before phosphatisation of their roots took place. A scenario for preferential phosphatisation of dicot roots is illustrated in Figure 3. 23. During a period of low organic input to the midden, a variety of plants (both monocots and dicots) colonise it and rapidly produce seeds which contribute the bulk of the midden seed bank. Significant deposition resumes and the plants are smothered and die. The monocot roots (lacking secondary thickening) decay rapidly but the more robust dicot roots remain in the soil. Conditions in the upper midden turn anoxic and mildly acidic, and rapid decay of the organic matter present takes place. Thus, the dicot roots and some of the seed bank are phosphatised. The monocot roots have long since completely disappeared.

A second anatomical difference between monocot and dicot roots may also be significant. The morphology of the vascular cylinders of the two groups is very different. In dicots, the centre of the cylinder is typically filled completely with vessels, clustered into two, three or four distinct

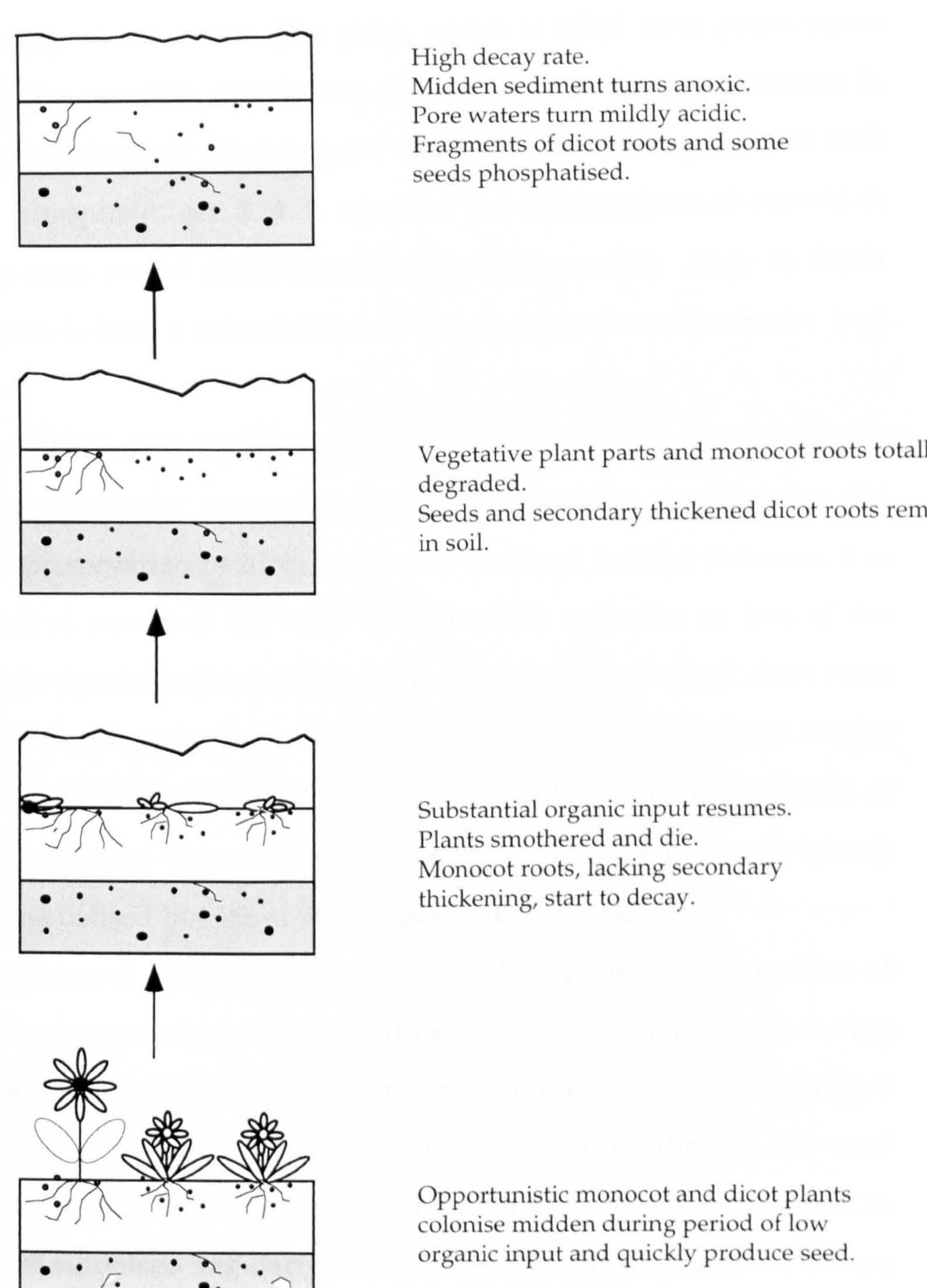


Figure 3. 23. Diagrams summarising a possible cycle of events that could result in preferential phosphatisation of dicot versus monocot roots.

groups (known as diarch, triarch and tetrarch roots respectively). The vascular vessels in monocot roots, on the other hand, are scattered throughout the central cylinder and in some cases there is a non-vascular gap in the centre (the pith), which is filled with parenchyma cells. If the vascular vessels are the main focus of mineralisation in roots (by conducting ion-rich pore waters and becoming infilled with calcium phosphate; see 3. 4. 3. 1.), then the arrangement of vessels in monocot roots would make them less likely to survive. Only in dicots do the vessels form a substantial structure in the centre of the root.

3. 4. 3. 2. 2. Differences in life cycle

In reconstructing preservational mechanisms to account for the selective preservation of dicot roots over monocot roots at Potterne, it is important to note that the roots of apparently only one or two of the many dicot species represented as seeds were fossilised. If all dicot roots had a greater phosphatisation potential, there should be a greater variety in the mineralised roots recovered. It is possible that the life habit of *certain* dicot roots favoured fossilisation, i.e. roots of perennial plants were phosphatised but those of annual plants were not.

The midden at Potterne was characterised by periods of deposition of organic-rich material, alternating with periods of less deposition, during which opportunistic plants (predominantly annuals) became established. A few perennials were among the colonisers contributing to the seed bank of the midden but it is not clear whether they persisted from year to year or re-colonised regularly along with the annual plants. Perhaps significantly, all the monocotyledons represented as seeds at Potterne are annual plants, whereas the dicots are a mixture of annual and perennial species. Two characteristics of perennial versus annual roots provide possible explanations for their preferential phosphatisation.

Firstly, the roots of annual plants tend to be relatively shallow, while perennial plants tend to root much deeper, for they may have to be securely anchored for several years. Selective mineralisation of the roots of perennial plants on the midden may reflect the fact that they reached depths in the sediment at which the conditions for phosphatisation were already developing. Hence, some of the deeper roots may have reached an environment in which it was too anoxic for them to survive, so they died and as they decayed, the high concentrations of ions released from decay of the plentiful organic remains in the midden facilitated their phosphatisation. However, it seems highly unrealistic to assume that roots would be found living under phosphatisation conditions, as they are sensitive to their surroundings and would avoid penetrating those areas of sediment that are inhospitable. However, the increased depth of the perennial roots may have placed them in an area of sediment where phosphatisation conditions developed much more quickly than in the shallower depths where the annuals rooted, enhancing the chances of the perennial roots surviving until they could become mineralised.

A second factor offering a more realistic reason for selective phosphatisation of perennial dicot roots is their greater robustness. Annual roots are less robust as they last only one year, while perennial roots persist in the soil for several years. Hence, after the plants growing on the midden were smothered, the roots of the annuals quickly decayed and disappeared. The perennials were also smothered but, although their subaerial parts died, their more robust roots persisted underground, ready to produce new shoots, should favourable conditions arise. Decay of the abundant organic matter that had been added to the midden eventually turned this area of the sediment anoxic and the high ion concentrations produced from decay allowed phosphatisation to take place. Some of the (predominantly annual) seed bank and the perennial

roots are phosphatised. The cycle is repeated a number of times, resulting in the preservation of phosphatised seeds and perennial roots throughout the depth of the Potterne midden.

3. 4. 3. 2. 3. Possible taxonomic identity of the Potterne root fragments

All the Potterne root fragments examined by Carruthers, Lawrence of the Jodrell Laboratory at Kew Gardens and the author appeared structurally very similar, suggesting that they all belong to only one or two species. Although it was not possible to identify the root fragments, their taxonomic identity can be constrained on the basis of three assumptions: (1) because the roots are found at all levels of the midden sampled, they must belong to a species that grew on the midden consistently throughout its history, and which is therefore presumably represented by mineralised seeds in all midden soil levels; (2) on the basis of their anatomy, the roots belong to dicotyledonous angiosperms with a diarch (i. e. 2 main vessel clusters) arrangement of their vascular tissue; and (3) because the roots represent only one or two of many dicot species present on the midden, they are assumed to be perennials with robust roots which could survive long enough to become mineralised, unlike their annual counterparts.

If it is assumed that the mineralised roots belong to a taxon represented by mineralised seeds found at all levels of the midden, this limits their taxonomic identity to just 5 perennial species and two additional genera which include both annuals and perennials (Table 3. 6.). The possibilities could be reduced further by eliminating those taxa that do not possess the same diarch arrangement of vascular vessels as the fossil roots. Unfortunately, an extensive literature search resulted only in the elimination of *Ranunculus* (which has a tetrarch arrangement) and the confirmation of *Sambucus nigra* (elder), which is

Genus/species:	Common name:	Life history:
Lithospermum officinale	Common Gromwell	Perennial
Myosotis sp.	Forget-me-nots	Annual/perenn
Sambucus nigra	Elder	Perennial
Ranunculus acris/bulbosus/repens	Buttercups	Perennial
Urtica dioica	Stinging nettle	Perennial
Urtica urens	Small nettle	Perennial
Atriplex/Chenopodium sp.	Oraches/goosefoots	Annual/perenn
Polygonum aviculare	Knotgrass	Annual

Table 3. 6. Life histories of the dicotyledonous taxa represented by mineralised seeds found at all soil levels sampled in the Potterne midden.

characterised by diarch roots, as a definite possibility. Carruthers (2000) singled out elder as one of the few perennials represented at Potterne likely to be robust enough to survive in parts of the midden where there was significant disturbance from waste disposal, making this species a realistic source of the Potterne root fragments. This question might be resolved in the future by obtaining root specimens of all of the taxa listed in Table 3. 6. and comparing their anatomical structure with the fossil root fragments.

CHAPTER 4. CLUSTER ANALYSIS OF PART OF THE FINDS DATABASE FOR THE ENVIRONMENTAL ARCHAEOLOGY UNIT, UNIVERSITY OF YORK.

4. 1. Introduction

This chapter analyses the associations of fossil taxa within different archaeological contexts through cluster analysis of a finds database maintained by Allan Hall at the Environmental Archaeology Unit (E. A. U.) of the University of York. The database contains comprehensive relative abundance data for the plant taxa recovered from archaeological samples processed by the E. A. U. over the past twenty years or so, along with more basic data on the vertebrate and invertebrate fossils recovered (see **4. 2. 1.** for full details of the data analysed). The aims of the cluster analysis were: (1) to identify groups of archaeological samples, and therefore depositional settings that preserve similar assemblages of taxa, and (2) to identify broad "taphonomic groups" of seed species which are likely to be preserved together if deposited under the same diagenetic conditions for the same period of time, in order to better understand the factors determining which taxa survive in different types of deposit. The rationale behind using this type of statistical analysis is that samples yielding broadly similar fossil assemblages will cluster together whilst those preserving few common taxa will be distant from each other in the dendrogram. Similarly, taxa which are typically found together in archaeological samples will be grouped together by cluster analysis, while those which rarely occur together in the same deposits will occupy distant clusters.

Biological remains from archaeological deposits are usually recovered in a charred, mineralised or organically preserved state. Charred or carbonised plant assemblages recovered from rural deposits are often

biased significantly towards cereal grains, due to their typical formation during crop processing. However, charred remains recovered in urban settings are often attributed to more general burning events. Charred plant remains can be recovered from a wide range of depositional settings because their relatively inert nature ensures that their long-term survival is less dependent on characteristics of the sediment in which they are deposited than are the other preservational states. The nature of the taphonomic biases inherent in organically preserved and mineralised assemblages are less clear and while deposits in the same broad depositional category might be expected to yield similar fossil assemblages, there may be significant variation within categories.

4. 2. Methods

4. 2. 1. The data analysed

The database from which data were selected for analysis was created and maintained by Allan Hall at the E. A. U., University of York, and contains details of the sub-fossil contents of the hundreds of samples recovered from contexts studied by the Unit over the past twenty or so years. Samples are typically processed by washing 1kg of sediment through a stack of sieves (apertures down to 300 microns) and examining both the sieve residues and the washover (i. e. those light remains that float on the surface of the water). Sub-samples of each of the sieve residues and the washover are examined under the binocular microscope and a semi-quantitative assessment made of the abundance of each taxon present (the relative abundance of each taxon present is estimated on a scale of 1 (very rare) to 4 (very abundant)). The complete E. A. U. database was unfeasibly large to analyse so it was necessary to select a (relatively) more manageable sub-set. A total of 139 samples were selected for analysis; all samples containing mineralised remains, including those in which the only

mineralised remains were faecal concretions, along with 19 samples completely lacking mineralised remains. It was reasoned that this selection criterion would ensure that the preservational trends of mineralised taxa could be identified, while the large number of samples totally lacking mineralised remains (19) or containing only mineralised faecal concretions would reveal taphonomic trends in dominantly organically preserved assemblages.

4. 2. 2. Clustering of samples

Before cluster analysis of the data was carried out, a number of measures were taken to ensure that the results obtained would give a reliable indication of the nature of preservation in archaeological deposits and not simply reflect biases inherent in the database. Firstly, to avoid any sampling bias introduced by variation in the processing method, all those samples which did not represent comprehensively examined 1 kg samples were removed from the database: for example, those comprising 1/2 kg samples, just sieve residues, just flots or "spot finds", i.e. one-off discoveries such as the plant remains found within an individual pot. While some taxa had just one type of entry in the database, others had multiple entries, representing preservation of different anatomical parts of the same species or the same part preserved in a different style (e. g. both mineralised and organically preserved). To prevent a disproportionate influence of such taxa on the outcome of clustering, all entries for each taxon were combined to give just one per taxon. In addition, although many contexts contained wood fragments, twigs and other non-taxonomically specific plant remains, it was decided to exclude these from the analysis as their taxonomic identity is unknown and they are likely to represent taxa already included in the database.

The database was also corrected by removing all dubious entries (those prefixed ? or cf.), giving a final total of 514 plant taxa along with 29 zoological entries (various bones and invertebrate remains) in 139 contexts, from 24 different sites (see Appendix 4 for the full data set analysed). Cluster analysis of the data was attempted using SYSTAT and MVSP but neither of these packages could deal with the large volume of data. Ultimately, the samples were clustered based on their contained fossil assemblages using SPSS for Windows (see **4. 2. 4.** for details). Two separate cluster analyses were carried out: one clustering the samples on the basis of the plants, invertebrates and vertebrate remains that they contain, and a second using only the data for plants.

4. 2. 3. Clustering of common seed and grain taxa

To gain an insight into which plant taxa tend to be preserved together in archaeological deposits, cluster analysis was carried out on the subset of data from the E. A. U. database for all common taxa (>5 occurrences) represented by whole seeds or grains. The cluster analysis was restricted to seeds and grains because these propagules represent the majority of easily identifiable plant fossils recovered from archaeological deposits, and because it is more straightforward to compare the preservation of such discrete entities than to consider the factors influencing the preservation of a range of disparate plant parts. As with the data analysed in the sample clustering, the database was corrected by omitting samples that had not been examined comprehensively. Taxa of uncertain identity (those prefixed ? or cf.), and records of plant remains other than seeds and grains were also omitted. Omission of non-propagule plant parts ensured that few multiple entries (different parts or preservational styles of the same taxon) remained in the database. These were retained to reveal any variation in the taxa occurring along with examples of the same taxa

preserved in different preservational styles (organically preserved/mineralised/charred). All taxon entries occurring less than 5 times were omitted from the database before analysis, as these might conceal associations between the more common taxa. The database that was analysed comprised 115 taxa in 139 contexts, from 24 different sites (see Appendix 4). Cluster analysis was carried out using SPSS for Windows.

4. 2. 4. Cluster analysis

The data were analysed using the Hierarchical Cluster facility of SPSS for Windows Version 9.0. Many of the "taxa" in the data set occur only relatively rarely, so that none of the similarity/distance measures available for analysing multistate data in SPSS was appropriate. All of these measures count mutual absences (double noughts in the database) as indicators of equal similarity to mutual presences, so that all rare entries would be treated incorrectly as very similar, on the basis of their shared absences from many samples. Therefore, the data were coded as additive binary data (so that 0 became 0000, 1 became 1000, 2 became 1100, 3 became 1110 and 4 became 1111) to allow the use of the Jaccard Coefficient, a measure of similarity for binary data which ignores all mutual noughts and considers only ones when calculating the similarity between two variables or cases. The Jaccard Coefficient can be summarised as

$$S = \frac{a}{a + b + c}$$

where a = no. of attributes occurring in both Case A and Case B, b = no. of attributes occurring in Case A but not in Case B, and c = no. of attributes occurring in Case B but not in Case A. The clustering algorithm chosen was the average linkage between groups (UPGMA), which is judged to be the best of the hierarchical clustering methods commonly employed in archaeological science (Wright, 1989; Baxter, 1994). With the UPGMA, the

similarity/dissimilarity between two groups equals the arithmetic average of the similarities between pairs of members in the two groups (Shennan, 1997).

4. 3. Results

4. 3. 1. Cluster analysis of contexts (samples) based on vertebrate, invertebrate and taxonomically identified plant remains

The results of the cluster analysis are presented as a dendrogram (Figure 4. 1..; fold-out page). On the largest scale, the samples in the dendrogram form two main clusters (**A** and **B**), each of which consists of several "sub-clusters". The uniting features of the samples in each sub-cluster are considered in turn, before discussing the common features of samples on a broader scale, within their major cluster. In the results below, the samples in the clusters are listed in tables according to their labels on the dendrogram (comprising their original spreadsheet column numbers), along with the category of deposit from which they were recovered (e.g. pit fill), their age, and the total number of fossil and named plant taxa recovered from them (n/n). The site/context codes for each sample number are listed in Table 4. 1., and the sites corresponding to the codes in Table 4. 2. Sub-cluster labels identify different parts of the dendrogram (Figure 4. 1.). The overall fossil diversity and number of plant taxa present in each sample are represented in Figures 4. 2. and 4. 3. The mean diversity of all the samples is marked on each graph to indicate whether diversity in a given sample is above or below average. These data are also represented as scatter graphs (Figures 4. 4. & 4. 5.) to facilitate easy comparison between the samples in the major clusters A and B. In all figures, the sample numbers are presented in the order that they appear on the dendrogram.

Figure 4. 1. Dendrogram produced by cluster analysis (using Jaccard Coefficient and average linkage between groups) of archaeological samples in the E. A. U., University of York finds database, based on their contained assemblages of biological remains.

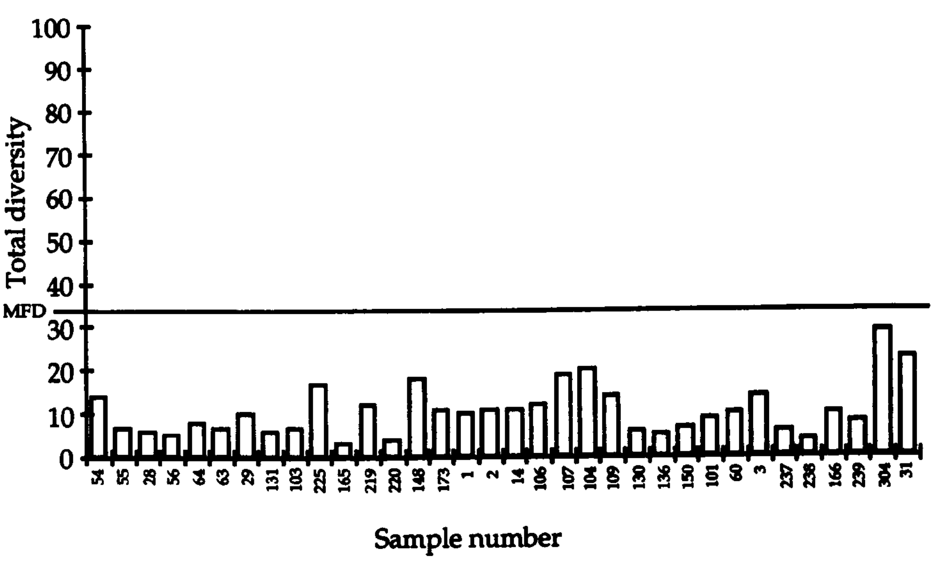
Sample no.	Site/Context	Sample no:	Site/Context
1	73-5.14/696	65	76-81.14/4493
2	73-5.14/697	69	76-7.15/379/14/T
3	73-5.14/1287	71	76-7.15/400
4	73-5.14/1482	75	76-7.15/506/1
5	73-5.14/1588	80	76-7.15/617
6	73-5.14/1747	96	78-9.8/3421
7	73-5.14/1748	97	78-9.8/3430
8	73-5.14/1749	98	78-9.8/3433
9	73-5.14/1750	101	75.6/3239
10	73-5.14/1758T	103	81.12/1108
12	73-5.14/1765	104	81.12/1109
13	73-5.14/1775	106	81.12/1114
14	73-5.14/1799T	107	81.12/1126
16	73-5.14/1903	108	81.12/1134
17	73-5.14/1908	109	81.12/1143
18	73-5.14/2007(151)	110	81.12/1162
19	73-5.14/2007(150)	130	85-6.9/1270
20	73-5.14/2115	131	85-6.9/1307
21	73-5.14/2118	132	85-6.9/1391
22	73-5.14/2121	136	85-6.9/4384
23	73-5.14/2139	148	85-6.9/10025
24	73-5.14/2172	150	85.5/67
25	73-5.14/2205	151	85.5/83
27	73-81.13/2006	152	85.5/111
28	73-81.13/2022	153	85.5/112
29	73-81.13/2050	156	94.321/1004
30	73-81.13/2070	157	94.321/1007
31	73-81.13/2166	158	94.321/1008
32	73-81.13/2269	159	94.321/1014
33	73-81.13/2439	160	94.321/1027
34	73-81.13/2573	161	94.321/1028
35	73-81.13/2961	162	94.321/1030
36	73-81.13/4093	163	94.321/1104
37	73-81.13/4134	164	94.321/1115
48	73-81.13/5466/584	165	94.321/8000
49	73-81.13/5466/591	166	95.434/105
50	73-81.13/5497	167	95.434/1053
52	73-81.13/6372	170	95.434/2037
54	73-81.13/7300T	171	95.434/3094
55	73-81.13/7300AT	173	95.434/3077
56	76-81.14/1095	174	BDF86/167
58	76-81.14/1384	175	BDF86/229
59	76-81.14/1437	185	BR11/11082
60	76-81.14/1456	189	BR11/11853
61	76-81.14/1479	193	DNB93-4/1495
62	76-81.14/4047	195	HAG93/20
63	76-81.14/4090	197	SELBY93/2084
64	76-81.14/4098	209	76-81.7/7216

Sample no.	Site/Context
210	76-81.7/8573
217	87.21/2166
218	88-9.17/1159
219	88-9.17/1204
220	88-9.17/1261
221	88-9.17/4068
225	89-90.28/3119
227	89-90.28/3217
231	89-90.28/3323
232	89-90.28/3410
233	89.6/52
234	90-1.29/2078
235	91.21/1079
237	97.102/2028
238	97.102/2031
239	98.02/2032
251	76-81.7/22490
285	76-81.7/30824
290	76-81.7/31167
304	87.21/2082/71
305	95.434/1059/15
306	95.434/1064/17
307	95.434/3105/105
308	BJT98/213/11
309	76-81.7/26631/1714(T)
310	73-81.13/2563/188(TP)
311	78-9.8/3475/162(T1)
312	88-9.17/4045/327(T1)
313	88-9.17/5035/451(T1)
314	89-90.24/72233/3541(T)
315	90-1.29/2046/2(T)
316	90-1.29/2050/4(T)
317	90-1.29/2076/8
318	90-1.29/2077/9(T)
319	91.21/1092/9(T)
320	95.434/1066/20(T)
321	95.434/1126/40(T)
322	95.434/3056/53(T)
323	95.434/3069/78(T)
324	95.434/3104/104(T)
325	95.434/3108/107(T)
326	95.434/3109/10801(T)
327	95.434/3109/10802(T)

Table 4.1. Site/context codes key, corresponding to sample numbers on dendrograms (Figures 4.1 and 4.6)

Sitecode	Area	Site name	Town	County
73-5.14	O	Skeldergate (post-Roman deposits)	York	NYR
73-81.13	I	Bedern (incl. Foundry)	York	NYR
73-81.13	X	Bedern (Vicars Choral), south-west	York	NYR
75.6		Blake St (9) (City Garage)	York	NYR
76-7.15		(site adjacent to) Aldwark (1-5)	York	NYR
76-81.14	I	Bedern (Vicars Choral), north-east	York	NYR
76-81.14	IV	Bedern (Vicars Choral), north-east	York	NYR
76-81.7		Coppergate (16-22)	York	NYR
78-9.8		Walmgate (118-26)	York	NYR
81.12		Rougier Street (5), York	York	NYR
85-6.9		Fishergate (46-54) (Redfearn's NG)	York	NYR
85.5		Aldwark (7-9)	York	NYR
87.21		Piccadilly (22) (ABC Cinema)	York	NYR
88-9.17		Micklegate (1-9) (Queens Hotel)	York	NYR
88.4		Trafalgar Bay, Nunnery Lane	York	NYR
89-90.28		Swinegate sites	York	NYR
90-1.29		17-21 Piccadilly (Reynard's Garage)	York	NYR
91.21		104-112 Walmgate (St Margaret's Churchyard)	York	NYR
94.3210		Parliament Street (44-5) (Curry's/M&S)	York	NYR
95.434		St Saviourgate	York	NYR
97.102		Davygate (British Gas)	York	NYR
BDF86		Dominican Friary/Priory	Beverley	HUM
BRII		The Brooks	Winchester	HMP
DNB93-4		North Bridge	Doncaster	SYR
SELBY93		Selby Town Centre	Selby	NYR

Table 4.2. The archaeological sites contributing to E.A.U., York finds database analysed using cluster analysis (NYR= North Yorksire, SYR= South Yorkshire, HUM= Humberside, HMP= Hampshire)



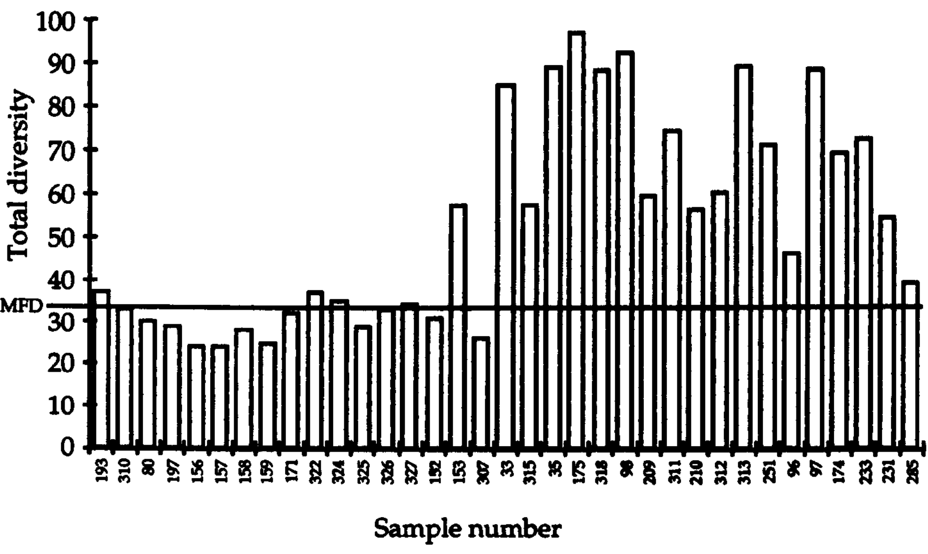
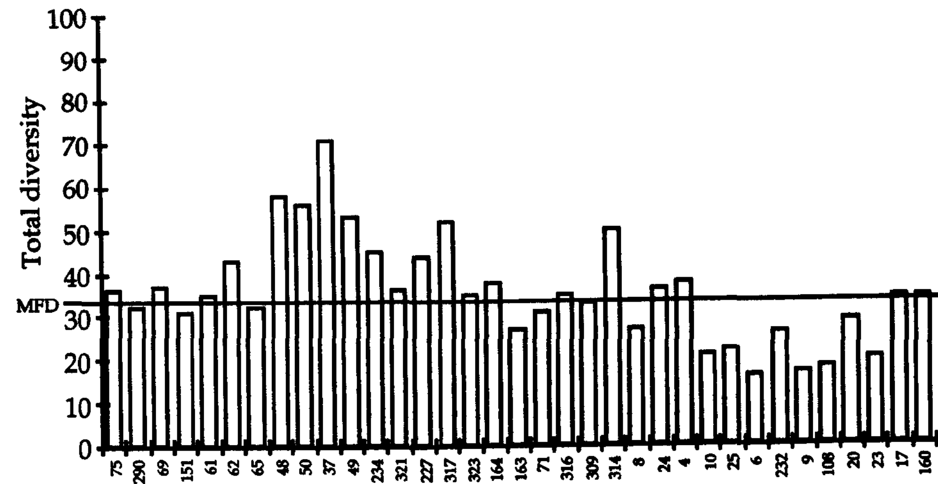
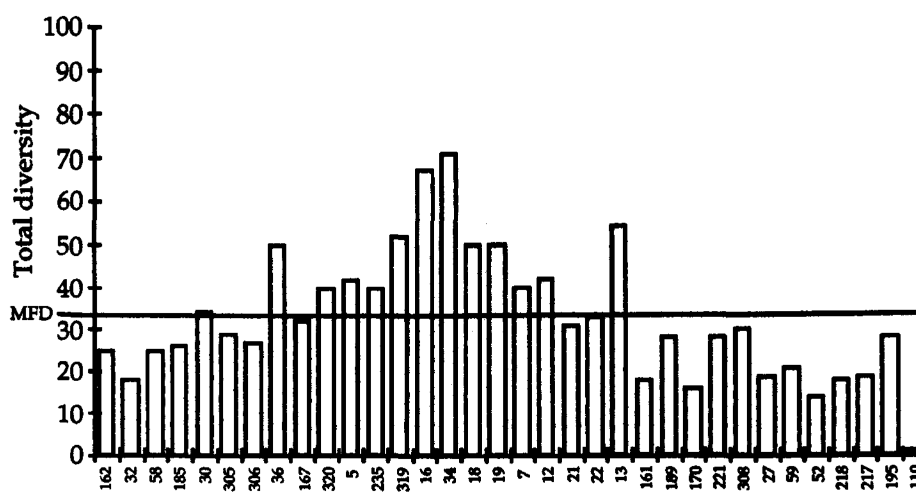


Figure 4. 2. Total numbers of fossil taxa present in samples processed by the Environmental Archaeology Unit, York. Sample numbers are shown in the order in which they appear in the dendrogram (Figure 4. 1.). The line labelled MFD indicates the mean fossil diversity, i.e. the mean number (34) of fossil taxa present in all of the samples analysed.





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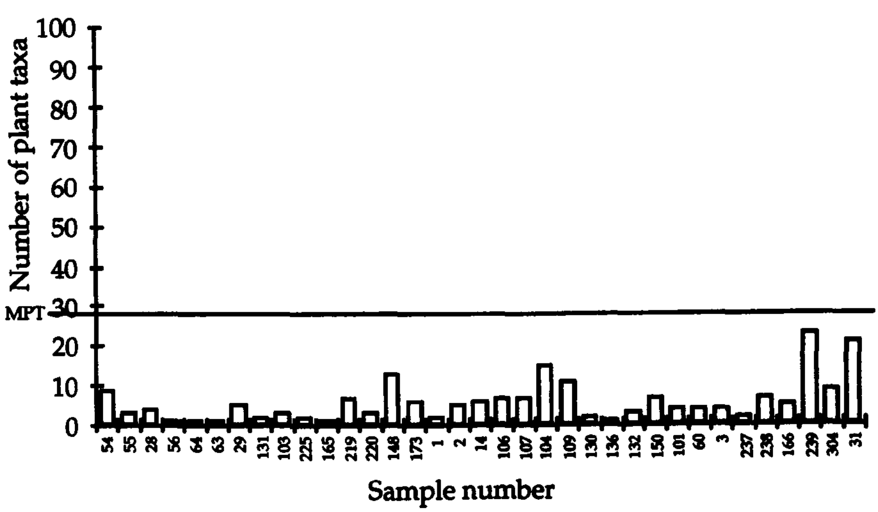


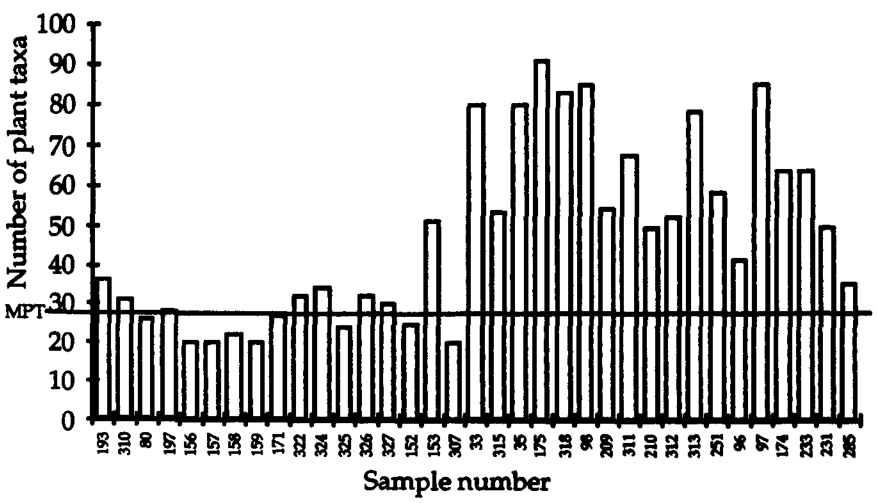
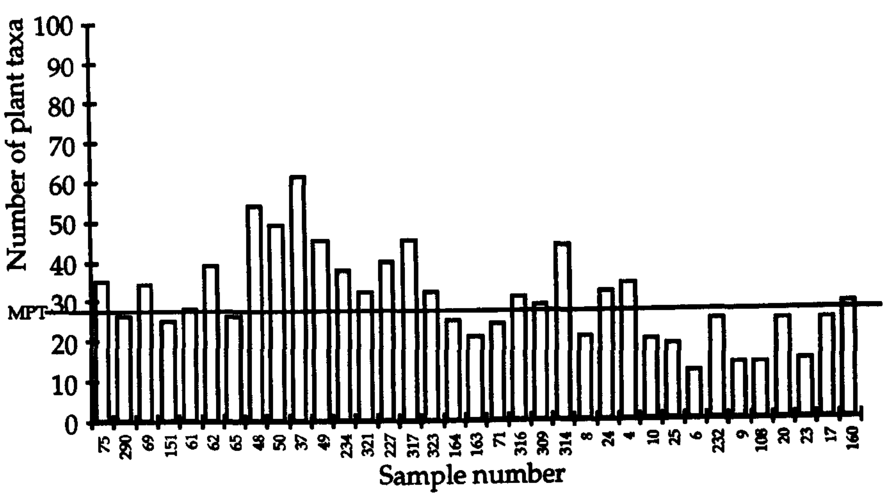


Figure 4. 3. Numbers of plant taxa recorded in samples processed by the Environmental Archaeology Unit, York. Sample numbers are in the order in which they occur in the dendrogram (Figure 4. 1). MPT indicates the mean number of plant taxa for all of the samples (27.5).



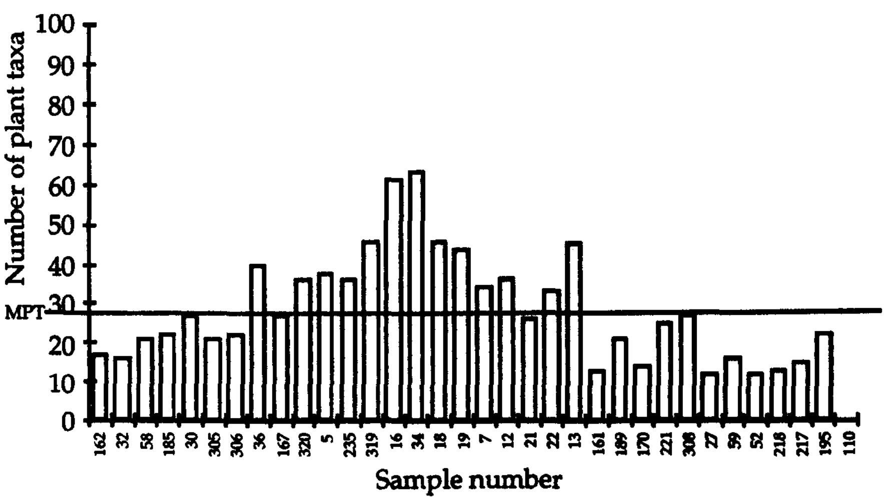


Figure 4. 3. ctd. Numbers of plant taxa recovered fromsamples processed by the Environmental Archaeology Unit, University of York, which were analysed using cluster analysis. Sample numbers are in the order in which they appear on the dendrogram (Figure). MPT indicates the mean number of plant taxa (27.5) recovered from the samples.

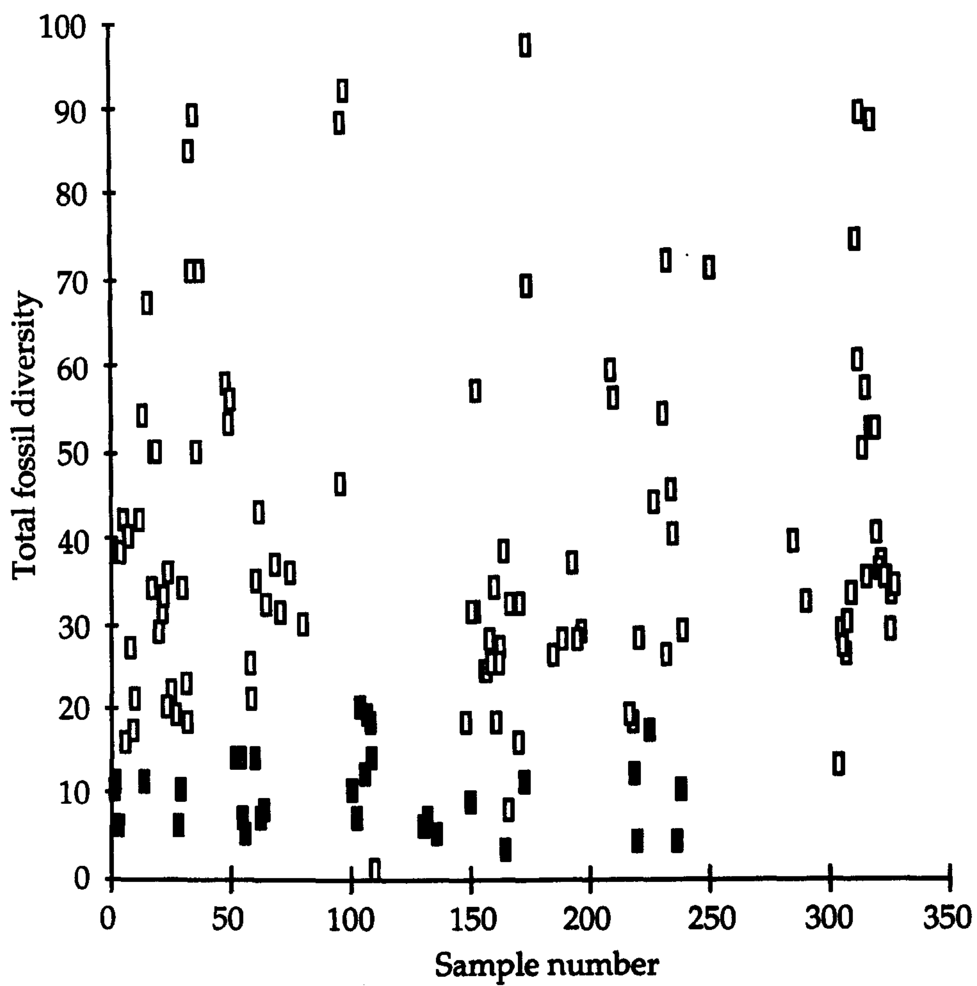


Figure 4. 4. Numbers of taxa recorded in the samples from the Environmental Archaeology Unit, York, analysed using cluster analysis (Dendrogram 4. 1.). Black rectangles represent samples falling within Cluster A in dendrogram.

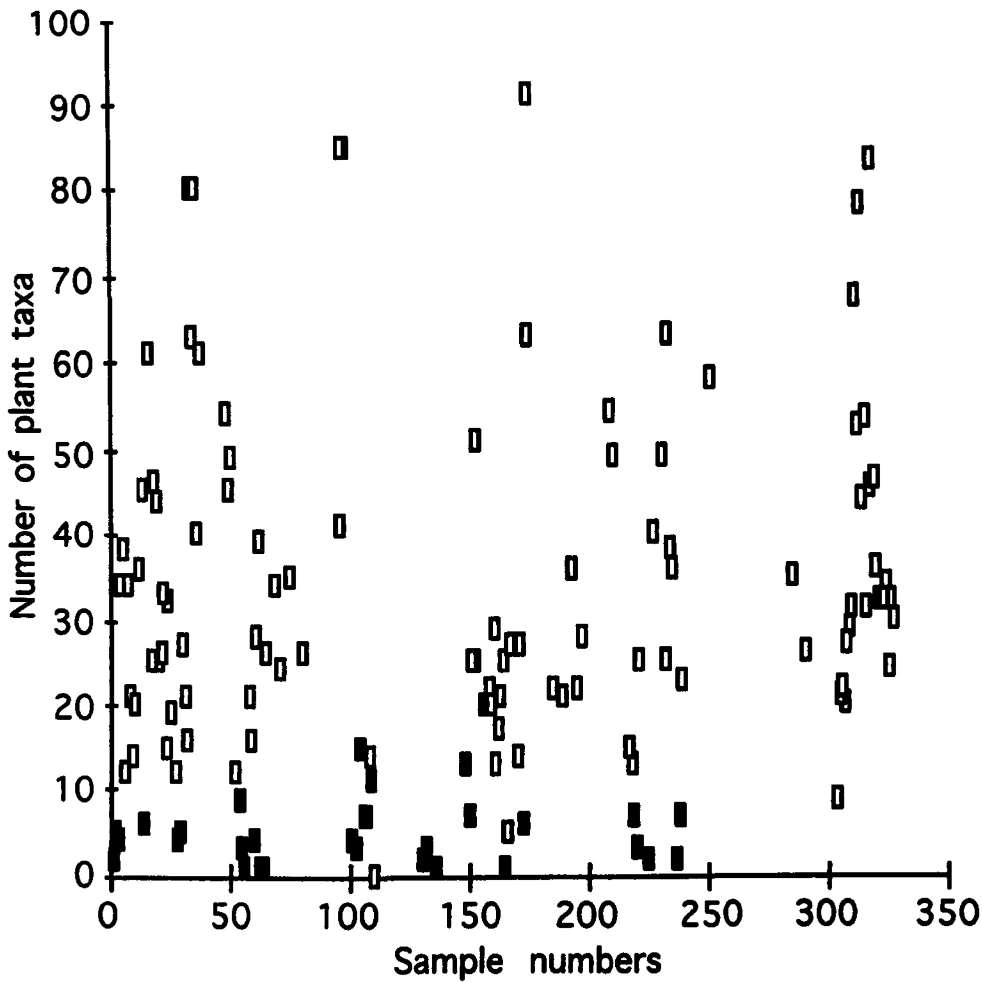


Figure 4. 5. Numbers of plant taxa recovered from samples processed by the Environmental Archaeology Unit, University of York, which were analysed using cluster analysis (Dendrogram 4. 1.). Black rectangles represent samples that lie within Cluster A in the dendrogram.

Major Cluster A

Cluster A comprises three constituent sub-clusters (i to iii), although the majority of samples lie in (i), which comprises a number of smaller clusters.

(i)(a) Part 1

This sub-cluster contains 18 samples:

Sample	Deposit type	Date	Total diversity	Plant taxa
54	pit fill	l.C14th - e. C15th	14	9
55	pit fill	l.C14th - e. C15th	7	3
28	pit fill	m.C15th - e.C17th	6	4
56	pit fill	mid. C17th	5	1
64	occupation layer	mid. C15th - e. C17th	8	1
63	pit fill	mid. C15th - e. C17th	7	1
29	pit fill	mid. C15th - e. C17th	10	5
131	pit fill	l.C7th-m.C9th	6	2
103	timber-lined pit fill	e.C13th	7	3
225	pit back fill	C13th-C14th	17	2
165	bore hole	?Medieval	3	1
219	barrel well fill	C10th	12	7
220	pit fill	C10th	4	3
148	post-hole fill	l.C7th-m.C9th	18	13
173	pit fill	Roman	11	6
1	stone-lined pit	?	10	2
2	stone-lined pit	?	11	5
14	pit fill	?	11	6

Fourteen of these 18 samples are pit fills, and the remainder were recovered from an occupation layer, a bore hole, a barrel well and a post-hole. The samples have a large age range, from the Roman period to the early 17th Century. They are all relatively impoverished in terms of plant fossil material but most contain animal fossils. No one plant taxon is found in all samples but 10 contain *Ficus carica* (fig) and 7 contain *Sambucus nigra* (elder). All but one sample contain bones and 12 have

both fish and mammal bones. 13 of the 18 samples contain mineralised material. The majority of these samples probably represent very degraded deposits which now retain only decay resistant or mineralised remains, although few biological remains are likely to have been present in the occupation layer, bore hole and post hole, as these deposits do not function as repositories for organic remains.

(i)(a) Part 2

This sub-cluster contains just 4 samples:

Sample	Deposit type	Date	Total diversity	Plant taxa
106	timber pit-lining	e. C13th	12	7
107	pit fill	e.C13th	19	7
104	timber pit-lining	e.C13th	20	15
109	pit fill	Anglo-Scandinavian	14	11

These pit fills were recovered from the same site and all but one are of the same age. The floras contained in the samples are relatively limited, although generally more diverse than those in **1(a) Part 1**. Only *Sambucus nigra* (elder) is found in all samples, although *Atriplex* sp(p). (oraches), *Avena* sp(p). (oats), *Brassica* sp(p). (cabbage, etc.), *Prunus* sp(p). (plum, sloe, etc.), *Juncus gerardi* (black rush), *Papaver argemone* (prickly poppy) and *Triticum/Secale* (wheat/rye "bran" fragments) are found in two of them. All of these samples contain mineralised remains and fish bone and only one lacks mammal bone.

(i) (b)

This sub-cluster contains 6 samples:

Sample	Deposit type	Date	Total diversity	Plant taxa
130	pit fill	l.C7th-m.C9th	6	2
136	?fire remains	e.-m.C14th	5	1
132	pit fill	C16th-C17th	7	3
150	pit fill	C13th-C14th	9	7
101	well fill	C13th-C14th	10	4
60	pit fill	l.C14th-e.C15th	14	4

These samples comprise 4 pit fills, a well fill and some possible fire remains. Four sites are represented and the samples cover quite a long time range, from the late 7th Century to the early 15th Century. All contain impoverished floras and no taxa are common to all. Half of the samples contain *Carex* sp(p). (sedges) and *Conium maculatum* (hemlock) and 4 contain *Sambucus nigra* (elder). Both fish and mammal bone are present in all of the samples, and mineralised remains are found in 4 out of the 6. Although these samples are united by the presence of similar scant fossil assemblages, as representatives of more than one deposit type, site and date, they are potentially the end points of a variety of different processes: burning (the possible fire), significant degradation (the pit fills and possibly the well fill) and limited original input (possibly the well).

A(ii)

This sub-cluster comprises just one sample:

Sample	Deposit type	Date	Total diversity	Plant taxa
3	cess pit?	?	6	4

This sample contains mineralised *Bilderdykia convolvulus* (black bindweed) and *Brassica* sp. (cabbage, etc.), organically preserved *Sambucus nigra* (elder) and charred *Rumex acetosella* (sheep's sorrel), along with bird and fish bone. This is more likely to represent a highly degraded deposit than one in which the original organic input was low, as many

more taxa would be expected even if this did not function as a cess pit and only received a background "rain" of weeds.

A(iii)

Sample	Deposit type	Date	Total diversity	Plant taxa
237	pit fill	C12th	4	2
238	dump	C12th	10	7

Although these samples are from the same period on the same site, they were recovered from different deposit types. Both yield an impoverished plant assemblage, of which only henbane (*Hyoscyamus niger*) is common to both, along with faecal concretions. Neither sample contains any mineralised remains although both contain bone fragments (1 indeterminate, 1 fish). The pairing of these samples is not very robust as it is based on the common presence of just henbane seeds and faecal concretions, which have a disproportionate influence due to the overall low fossil diversity of the samples.

Cluster A overall

All samples in Cluster A contain impoverished plant assemblages, with diversities significantly below the mean for all of the samples analysed. The majority of the samples in Cluster A are likely to represent the decay-resistant remains of very degraded deposits, an inference based on the assumption that, regardless of their original anthropogenic function, all archaeological deposits would have originally contained a relatively diverse "background" assemblage of weeds. Twenty-two of the 31 contexts contain mineralised fossil remains, and bones are present in all but 1.

Major Cluster B

B2 forms an out-group to the numerous other samples in this major cluster:

Sample	Deposit type	Date	Total diversity	Plant taxa
110	layer	C4th	1	0

This sample contains just fish bone so its distance from the other samples in the dendrogram is unsurprising.

The remaining samples in Major Cluster B (**B1**) lie within 5 sub-clusters (i to v), with (iii) containing the majority.

B1(i)

Sample	Deposit type	Date	Total diversity	Plant taxa
166	hollow	late Medieval	8	5
304	?	?	13	9
239	dump	C11th-C12th	29	23

These samples lack mineralised remains (except faecal concretions) and have two taxa in common, *Urtica dioicai* (stinging nettle) and *Viola* sp. (violet), in addition to bone fragments.

B1(ii)

This sub-cluster comprises just one sample:

Sample	Deposit type	Date	Total diversity	Plant taxa
31	organic layer	l.C14th-l.C15th	23	21

This sample, from an organic layer, yielded mineralised corncockle (*Agrostemma githago*), as well as 20 organically preserved plant taxa,

faecal concretions and fish bone. Its overall fossil and plant diversities are lower than average.

B1(iii)

Part 1

Sample	Deposit type	Date	Total diversity	Plant taxa
193	oven	C13th	37	36
310	pit fill	m.-l.C14th	33	31

These samples represent two different sites, ages and deposit types but still yield a number of the same plant taxa: *Agrostemma githago* (corncockle), *Anthemis cotula* (stinking chamomile), *Atriplex* sp(p). (oraches), *Avena* sp(p). (oats), *Bilderdykia convolvulus* (black bindweed), *Bromus* sp(p). (bromes), *Carex* sp(p). (sedges), *Centaurea* sp(p). (knapweeds), *Chrysanthemum segetum* (corn marigold), Gramineae (grasses), *Prunella vulgaris* (selfheal), *Rumex acetosella* agg. (sheep's sorrel) and *Rumex* sp(p). (docks). However, the majority of these taxa are charred oven remains so direct preservational comparison cannot be made with the pit fill. One mineralised taxon (corncockle seed fragments) is present in the oven remains as well as fish bone. The overall and plant fossil diversities of these samples are close to the mean for all of the samples.

Part 2

Sample	Deposit type	Date	Total diversity	Plant taxa
80	?	post-Conquest Medieval	30	26
197	?ditch fill	Medieval	29	28

These samples, from two different sites, are both of dubious provenance and rather broad date. The samples contain slightly below average diversities of fossils with nine taxa common to both: *Anthemis cotula* (stinking chamomile), *Atriplex* sp(p). (oraches), *Carex* sp(p). (sedges), *Fragaria vesca* (strawberry), *Polygonum persicaria* (redshank), *Quercus* sp(p). (oak), *Raphanus raphanistrum* (wild radish pod segments/fragments), *Sambucus nigra* (elder) and *Urtica dioica* (stinging nettle).

Sample 197 contains 1 mineralised taxon (*Brassica* sp./*Sinapis arvensis*; cabbages, etc./charlock) along with indeterminate bone fragments. Sample 80 lacks mineralised remains.

Part 3

(a)

Sample	Deposit type	Date	Total diversity	Plant taxa
156	?pit fill	?post-Conquest Medieval	24	20
157	fill	m.C11th-m.C13th	24	20
158	fill	m.C11th-m.C13th	28	22
159	fill	C11th-C12th	25	20

These fills are all from the same site and possibly the same age as the three dated fills lie within the post-Conquest Medieval period (1066-1500). The samples contain below average total and plant diversities, including 6 taxa which are found in all, along with beetles and fly puparia: *Agrostemma githago* (corncockle), *Atriplex* sp(p). (oraches), *Polygonum persicaria* (redshank), *Reseda luteola* (weld), *Rumex acetosella* (sheep's sorrel) and *Sphagnum imbricatum* (*Sphagnum* moss).

In addition, 3 of the samples contain *Brassica rapa* (turnip), *Chenopodium* Section *Pseudoblitum* (goosefoots), *Ficus carica* (fig), *Juncus bufonius* (toad rush), *Sambucus nigra* (elder), *Silene vulgaris* (bladder campion) and *Stellaria media* (common chickweed), and half contain *Carex* sp(p). (sedges), *Papaver somniferum* (prickly poppy), *Polygonum aviculare* (knotgrass), *Ranunculus* Section *Ranunculus* (buttercups), *Rubus fruticosus* (blackberry) and *Silene alba* (white campion) along with faecal concretions and fish bone.

(b)

This sub-cluster contains the majority of samples in Cluster B, and comprises a number of smaller clusters, which are discussed in turn below.

Sample	Deposit type	Date	Total diversity	Plant taxa
171	pit fill	Anglo-Scandinavian	32	27
322	pit fill	Anglo-Scandinavian	37	32
324	pit fill	Anglo-Scandinavian	35	34
325	pit fill	Anglo-Scandinavian	29	24
326	pit fill	Anglo-Scandinavian	33	32
327	pit fill	Anglo-Scandinavian	34	30

These 6 samples are all Viking pit fills recovered from St. Saviourgate. The contained floras are all close to the mean diversity for all samples and 8 taxa are common to all samples: *Atriplex* sp(p). (oraches), *Chenopodium album* (fat hen), *Chenopodium* Section *Pseudoblitum* (goosefoots), *Polygonum aviculare* (knotgrass), *Sambucus nigra* (elder), *Stellaria media* (common chickweed), *Urtica dioica* (stinging nettle) and *Urtica urens* (small nettle).

In addition, 5 samples contain: *Agrostemma githago* (corncockle), *Carex* sp(p). (sedges), *Corylus avellana* (hazel), *Rumex* sp(p). (docks), *Scorpidium scorpioides* (a moss) and mammal bone.

Four of the samples contain: *Arctium* sp(p). (burdock), bone fragments and earthworm egg caps.

Half of the samples contain: *Anthemis cotula* (stinking chamomile), *Capsella bursa-pastoris* (shepherd's-purse), Gramineae (grasses), *Hyoscyamus niger* (henbane), *Potentilla* sp(p). (cinquefoils), *Prunella vulgaris* (selfheal), *Ranunculus flammula* (lesser spearwort), *Ranunculus sceleratus* (celery-leaved buttercup), *Ranunculus sardous* (hairy buttercup), *Ranunculus* Section *Ranunculus* (buttercups), *Sonchus asper* (prickly sow-thistle), *Sphagnum* Section *Acutifolia* (*Sphagnum* moss) and *Triticum/Secale* (wheat/rye "bran" fragments).

None of the samples contains any mineralised material.

Sample	Deposit type	Date	Total diversity	Plant taxa
152	pit fill	?Anglo-Scandinavian	31	25
153	pit fill	?Anglo-Scandinavian	57	51
307	pit fill	?C4th	26	20

These 3 pit fills represent 2 different sites and are of dubious age but may represent the range of dates from the 4th Century to Anglo-Scandinavian (9th - 11th Century). Sample 153 preserves an above average diversity but the other two are of average diversity. Five taxa are common to all, along with eggshell membrane fragments and fly puparia: *Anagallis arvensis* (scarlet pimpernel), *Atriplex* sp(p). (oraches), *Conium maculatum* (hemlock), *Rubus fruticosus* (blackberry) and *Sambucus nigra* (elder).

In addition, 2 out of 3 samples contain: *Aethusa cynapium* (fool's parsley), *Carex* sp(p). (sedges), *Chenopodium polyspermum* (many-seeded goosefoot), *Chenopodium* Section *Pseudoblitum* (oak-leaved/red goosefoot), *Hyoscyamus niger* (henbane), *Malus sylvestris* (crab apple; 1 sample just endocarp), *Potentilla erecta* (tormentil), *Prunus* sp(p). (plum, peach, etc.), *Ranunculus sceleratus* (celery-leaved buttercup), *Ranunculus* Section *Ranunculus* (buttercups), *Rubus idaeus* (raspberry), *Rumex* sp(p). (docks), *Solanum nigrum* (black nightshade), *Stellaria media* (common chickweed), faecal concretions, fish bone and mammal bone.

Sample	Deposit type	Date	Total diversity	Plant taxa
33	pit fill	l.C14th-e.C15th	85	80
315	pit fill	l.C14th	57	53
35	basal pit fill	m.-l.C13th	89	80
175	pit fill	?C12th-C14th	97	91
318	pit fill	l.C12th-e.C13th	88	83
98	backfill of robbed bedding trench	C11th-C12th	92	85

These samples were recovered from 4 different sites, although, with one exception, they are pit fills of similar age. The contained floras are all very diverse and a number of taxa are common to all samples: *Agrostemma githago* (corncockle), *Carex* sp(p). (sedges), *Ranunculus* Section *Ranunculus* (buttercups), *Rumex* sp(p). (docks), *Rumex acetosella* (sheep's sorrel), *Spergula arvensis* (corn spurrey) and *Triticum/Secale* (wheat/rye "bran" fragments), along with fish bone and fly puparia.

In addition, 5 samples contain: *Anthemis cotula* (stinking chamomile), *Calliergon cuspidatum* (a moss), *Centaurea* sp(p). (knapweeds), *Chenopodium album* (fat hen), *Chrysanthemum segetum* (corn marigold), *Eleocharis palustris* (common spike-rush), *Galeopsis* Subgenus

Galeopsis (hemp nettles), *Heracleum sphondylium* (hogweed), *Lapsana communis* (nipplewort), *Leontodon* sp(p). (hawkbits), *Linum usitatissimum* (flax), *Raphanus raphanistrum* (wild radish), *Sphagnum* sp(p). (*Sphagnum* moss), *Stellaria media* (common chickweed) and *Urtica urens* (small nettle).

Four samples contain: *Anthriscus sylvestris* (cow parsley), *Atriplex* sp(p). (oraches), *Avena* sp(p). (oats), *Brassica* sp. (cabbages, etc.), *Brassica* sp./*Sinapis arvensis* (cabbages, etc./charlock), *Brassica rapa* (turnip), *Calliergon giganteum* (a moss), *Calluma vulgaris* (heather), Cerealia indet. (cereals), Gramineae (grasses), Gramineae/Cerealia (grasses/cereals), *Hypnum cupressiforme* (a moss), *Hypochoeris* sp(p). (cat's ears, etc.), *Malus sylvestris* (crab apple; 3 samples just endocarp), *Polygonum aviculare* (knotgrass), *Polygonum lapathifolium* (pale persicaria), *Polygonum persicaria* (redshank), *Prunella vulgaris* (selfheal), *Rhinanthus* sp(p). (yellow rattle, etc.), *Rubus fruticosus* (blackberry), *Salix* sp(p). (willow), *Scandix pecten-veneris* (shepherd's needle), *Senecio* sp(p). (ragworts), *Silene vulgaris* (bladder campion) and *Urtica dioica* (stinging nettle).

Half of the samples contain: *Aethusa cynapium* (fool's parsley), *Agrostis* sp(p). (bentgrass), *Caltha palustris* (marsh marigold), *Corylus avellana* (hazel), *Juncus bufonius* (toad rush), *Plantago major* (greater plantain), *Potentilla erecta* (tormentil), *Sphagnum imbricatum* (*Sphagnum* moss), and beetles.

Sample	Deposit type	Date	Total diversity	Plant taxa
209	floor	c.975-e.-m.C11th	59	54
311	pit fill	C11th	74	67
210	yard deposit	c.930-5-c.975	56	49
312	pit fill	C10th-C11th	60	52
313	pit fill	C10th-C11th	189	78

251	fill in feature in building	c.930-5-c.975	71	58
96	floor	C11th-C12th	46	41
97	?	C11th-C13th	88	85

These samples represent 3 different sites and comprise 3 pit fills, 2 floor deposits, a yard deposit, a fill in a feature in a building and an indeterminate sample, all approximately equivalent in age. All 8 samples contain above average to very diverse plant assemblages, of which 7 taxa are common to all, along with fly puparia: *Atriplex* sp(p). (oraches), *Bilderdykia convolvulus* black bindweed?), *Carex* sp(p). (sedges), *Chenopodium album* (fat hen), *Eleocharis palustris* (common spike-rush), *Raphanus raphanistrum* (wild radish) and *Sambucus nigra* (elder).

In addition, 7 samples contain: *Agrostemma githago* (corncockle), *Anthemis cotula* (stinking chamomile), *Corylus avellana* (hazel), *Galeopsis* Subgenus *Galeopsis* (hemp nettles), *Hyoscyamus niger* (henbane), *Polygonum aviculare* (knotgrass) and fish bone.

Six samples contain: *Aethusa cynapium* (fool's parsley), *Brassica rapa* (turnip), *Homalothecium sericeum/lutescens* (a moss), *Hypnum cupressiforme* (a moss), *Juncus bufonius* (toad rush), *Lapsana communis* (nipplewort), *Linum usitatissimum* (flax), *Neckera complanata* (a moss), *Rumex* sp(p). (docks), *Sonchus asper* (prickly sow-thistle), *Thuidium tamariscinum* (a moss), *Urtica urens* (small nettle), *Viola* sp(p). (violet), along with beetles and bone fragments.

Five samples contain: *Avena* sp(p). (oats), *Brassica* sp./*Sinapis arvensis* (cabbage, etc./charlock), *Diphasium complanatum* (Issler's clubmoss), *Malus sylvestris* (crab apple), *Ranunculus* Section *Ranunculus* (buttercups), *Valerianella dentata* (narrow-fruited cornsalad) and earthworm egg caps.

Half of the samples contain eggshell membrane fragments, along with: *Antitrichia curtipendula* (a moss), *Calliergon giganteum* (a moss), *Carduus/Cirsium* sp(p). (thistle), *Genista tinctoria* (dyer's greenweed), Gramineae (grasses), *Hordeum* sp(p). (barley), Leguminosae (legumes), *Potentilla erecta* (tormentil), *Rubus fruticosus* (blackberry), *Rumex acetosella* (sheep's sorrel), *Spergula arvensis* (corn spurrey), *Triticum/Secale* (wheat/rye "bran" fragments) and *Triticum aestivo-compactum* (bread wheat).

Two of the samples (209 and 251) contain a limited mineralised component (1 and 2 taxa respectively), along with fish bone.

Sample	Deposit type	Date	Total diversity	Plant taxa
174	upper fill of u-shaped feature	?C12th-C14th	69	63

This sample lacks mineralised remains but contains a diverse assemblage of 63 organically preserved plant taxa, along with *Ascaris* and *Trichuris* ova, earthworm egg caps, faecal concretions, fly puparia and snails.

Sample	Deposit type	Date	Total diversity	Plant taxa
233	?	?	72	63

This indeterminate sample of unknown age contains 63 organically preserved plant taxa, along with beetles, caddis fly larva cases, *Daphnia* ephippia, fish bone, fly puparia, mammal bone, rat-tailed maggot (respiratory processes), slug granules and snails.

Sample	Deposit type	Date	Total diversity	Plant taxa
231	backfill of pit cut	C11th-C12th	54	49
285	external layer	m.C9th-e.C10th	39	35
75	pit fill	C11th	36	35
290	pit fill	l.C9th-c.930-5	32	26

These samples represent three different sites and comprise 2 pit fills, an external layer and a backfill of a pit cut. The samples cover a range of ages from the 9th to the 11th Century.

While sample 231 is relatively diverse, the diversity of the others is average. All 4 samples contain: *Agrostemma githago* (corncockle), *Chenopodium album* (fat hen), *Hyoscyamus niger* (henbane), *Lapsana communis* (nipplewort), *Malus sylvestris* (crab apple), *Polygonum persicaria* (redshank), *Urtica dioica* (stinging nettle) and *Urtica urens* (small nettle), as well as faecal concretions.

Three samples contain: *Anthemis cotula* (stinking chamomile), *Atriplex* sp(p). (oraches), *Brassica rapa* (turnip), *Corylus avellana* (hazel), *Ranunculus* Section *Ranunculus* (buttercups), *Sambucus nigra* (elder) and *Stellaria media* (common chickweed), along with fly puparia.

A number of other taxa were found in half of the samples. None of the samples yielded any mineralised remains.

Sample	Deposit type	Date	Total diversity	Plant taxa
69	bank	C12th-C14th	37	34
151	pit fill	C13th-C14th	31	25

These samples are from different sites and of different types, although they may overlap in age. Both samples contain average fossil diversities and yield a limited mineralised component (1 and 2 taxa), along with fish and mammal bone. Fourteen taxa are found in both samples: *Anthemis*

cotula (stinking chamomile), *Atriplex* sp(p). (oraches), *Brassica rapa* (turnip), *Carex* sp(p). (sedges), *Danthonia decumbens* (heath grass), *Eleocharis palustris* (common spike-rush), *Juncus* sp(p). (rushes), *Lapsana communis* (nipplewort), *Ranunculus flammula* (lesser spearwort), *Ranunculus sceleratus* (celery-leaved buttercup), *Ranunculus* Section *Ranunculus* (buttercups), *Rumex acetosella* (sheep's sorrel), *Sambucus nigra* (elder) and *Viola* sp(p). (violet).

Sample	Deposit type	Date	Total diversity	Plant taxa
61	pit fill	l.C14th-e.C15th	35	28
62	pit fill	m.C15th-e.C17th	43	39
65	pit fill	e.-m.C13th	32	26
48	pit fill	m.-l.C14th	58	54
50	pit fill	m.-l.C14th	56	49
37	pit fill	e.C14th	71	61
49	pit fill	m.-l.C14th	53	45

These samples are from 2 different sites and are all pit fills dating from between the early 13th and early 17th Centuries. Three of the samples (48, 50 and 37) contain a very limited mineralised component (2, 1 and 2 taxa respectively), along with both fish and mammal bones. The samples contain average to fairly diverse floras and 6 taxa are common to all, along with fish and mammal bone: *Carex* sp(p). (sedges), *Chenopodium album* (fat hen), *Ficus carica* (fig), *Rumex acetosella* (sheep's sorrel), *Sphagnum* sp(p). (*Sphagnum* moss) and *Urtica dioica* (stinging nettle).

In addition, 6 samples contain: *Agrostemma githago* (corncockle), *Atriplex* sp(p). (oraches), *Bilderdykia convolvulus* black bindweed), *Eleocharis palustris* (common spike-rush), *Rumex* sp(p). (docks), *Sambucus nigra* (elder) and *Stellaria media* (common chickweed) along with faecal concretions and fly puparia.

Five samples contain: *Brassica rapa* (turnip), *Chrysanthemum segetum* (corn marigold), *Fragaria vesca* (wild strawberry), *Juncus bufonius* (toad rush), *Polygonum lapathifolium* (pale persicaria), *Polygonum persicaria* (redshank), *Ranunculus* Section *Ranunculus* (buttercups) and *Raphanus raphanistrum* (wild radish).

Sample	Deposit type	Date	Total diversity	Plant taxa
234	silt layer	C12th	45	38
321	pit fill	C14th	36	32
227	dump	C12th-C13th	44	40
317	pit fill	e.-m.C13th	52	45
323	pit fill	Anglo-Scandinavian	35	32
164	?pit fill	?post-Conquest Medieval	38	25
163	?pit fill	?post-Conquest Medieval	27	21

These samples represent 4 different sites and comprise 5 pit fills, a silt layer and a dump. The samples contain average to relatively diverse floras, of which 3 taxa are common to all: *Agrostemma githago* (corncockle), *Ranunculus* Section *Ranunculus* (buttercups) and *Urtica dioica* (stinging nettle).

In addition, 6 samples contain: *Carex* sp(p). (sedges), *Atriplex* sp(p). (oraches), *Chenopodium album* (fat hen), *Stellaria media* (common chickweed) and earthworm egg caps.

Five samples contain: *Aethusa cynapium* (fool's parsley), *Brassica rapa* (turnip), *Corylus avellana* (hazel), *Polygonum persicaria* (redshank), *Rumex* sp(p). (docks), *Anthemis cotula* (stinking chamomile), *Chenopodium* Section *Pseudoblitum* (goosefoots), *Chrysanthemum segetum* (corn marigold), *Eleocharis palustris* (common spike-rush), *Juncus bufonius* (toad rush), *Reseda luteola* (weld), *Polygonum aviculare*

(knotgrass), *Ranunculus sceleratis* (celery-leaved buttercup), bone fragments and fish bone.

Four samples contain: *Centaurea* sp(p). (knapweeds), *Urtica urens* (small nettle), *Lapsana communis* (nipplewort), *Linum usitatissimum* (flax), *Polygonum lapathifolium* (pale persicaria), *Ranunculus sardous* (hairy buttercup), *Sambucus nigra* (elder), fly puparia and fish scales.

Only one sample (234) contains any mineralised taxa (1:), along with fish and mammal bone.

Sample	Deposit type	Date	Total diversity	Plant taxa
71	pit in bank	C12th-C14th	31	24
316	pit fill	m.C13th-C14th	35	31

These two pit fills are of approximately equivalent age and were recovered from different sites. The samples both contain slightly below average diversity plant assemblages, of which 9 taxa are common to both, along with fish and mammal bone: *Agrostemma githago* (corncockle), *Atriplex* sp(p). (oraches), *Chenopodium album* (fat hen), *Eleocharis palustris* (common spike-rush), *Juncus bufonius* (toad rush), *Ranunculus* Section *Ranunculus* (buttercups), *Sambucus nigra* (elder), *Scandix pecten-veneris* (shepherd's needle) and *Urtica urens* (small nettle).

Sample 71 contains 1 mineralised taxon but 316 totally lacks mineralised remains.

Sample	Deposit type	Date	Total diversity	Plant taxa
309	pit fill	Anglo-Scandinavian	33	29

This pit fill contains an average diversity plant assemblage, along with fish bone, fly puparia, mammal bone and oyster shells. No mineralised remains are present.

Sample	Deposit type	Date	Total diversity	Plant taxa
314	pit fill	m.-l.C2nd	50	44

This is a pit fill containing a relatively diverse plant assemblage, as well as beetles, bone fragments, earthworm egg caps, fly puparia, mammal teeth and oyster shell fragments. No mineralised remains are present.

B1 Part 3(c)

Sample	Deposit type	Date	Total diversity	Plant taxa
8	pit fill	?	27	21
24	pit fill	?	36	32
4	pit fill	?	38	34
10	pit fill	?	21	20
25	pit fill	?	22	19
6	pit fill	?	16	12
232	dump	C11th-C12th	26	25

All but one of these 7 samples are pit fills of indeterminate age recovered from the same site. The remaining sample was recovered from a 11th to 12th Century dump. The samples all yield average or below average floral and fossil diversities, and *Agrostemma githago* (corncockle) is the only taxon found in all. Six out of 7 samples contain faecal concretions and mammal bone. Fish bone is present in 5 of the samples, along with the plants *Brassica rapa* (turnip), *Centaurea* sp(p). (knapweeds),

Lapsana communis (nipplewort), *Malus* sp(p). (apple) and *Urtica urens* (small nettle).

In addition, 4 samples contain *Atriplex* sp(p). (oraches), *Galeopsis* Subgenus *Galeopsis* (hemp nettles), *Lamium* Section *Lamiopsis* (dead nettles), *Linum usitatissimum* (flax), *Polygonum lapathifolium* (pale persicaria), *Polygonum hydropiper* (water pepper), *Prunus spinosa* (blackthorn), *Rubus fruticosus* (blackberry), *Rumex acetosella* (sheep's sorrel) and *Sambucus nigra* (elder).

Three of the samples (10, 25 and 232) contain a very limited mineralised component (1 taxon each) and of these, only sample 10 lacks bones.

Sample	Deposit type	Date	Total diversity	Plant taxa
9	pit fill	?	17	14
108	pit fill	e.C13th	18	14
20	pit fill	?	29	25
23	?floor	?	20	15
17	?pit/trench/floor	?	34	25
160	fill	?	34	29
162	fill	C11th-C12th	25	17

These samples comprise 3 pit fills, a possible floor deposit and three indeterminate fills, and represent three different sites. The fossil assemblages are of below average diversity, and corncockle (*Agrostemma githago*) is the only plant found in all of the samples. Six of the seven samples yield *Sambucus nigra* (elder), fish bone and faecal concretions. Mammal bone and fly puparia are present in 5 of the samples, as are the plants *Atriplex* sp(p). (oraches), *Eleocharis palustris* (common spike-rush), *Juncus bufonius* (toad rush), *Rubus fruticosus* (blackberry), *Triticum/Secale* (wheat/rye "bran") and *Urtica dioica* (stinging nettle). Four samples yielded *Carex* sp(p). (sedges), *Chenopodium album* (fat hen) and *Urtica urens* (small nettle), and eggshell fragments.

Four of the samples (108, 20, 23 and 17) contain a limited mineralised component (1 taxon in 20, 2 in the rest), along with fish and mammal bone in all but 108, in which all the bone is mammal.

Sample	Deposit type	Date	Total diversity	Plant taxa
32	floor	e.-m.C14th	18	16
58	pit fill	l.C14th-e.C15th	25	21
185	well fill	l.C14th-C16th	26	22
30	basal pit fill	m.C15th-e.C17th	34	27

These samples represent three different sites and comprise two pit fills, a well fill and a floor deposit, covering a fairly restricted period (early 14th to early 17th Century). The samples contain plant assemblages of average or (usually) below average diversity, with three taxa common to all, along with faecal concretions and fish bone: *Agrostemma githago* (corncockle), *Ficus carica* (fig) and *Vitis vinifera* (vine/grape). Fly puparia are present in 3 samples, as are *Foeniculum vulgare* (fennel), *Fragaria vesca* (wild strawberry), *Rubus fruticosus* (blackberry) and *Triticum/Secale* (wheat/rye "bran" fragments). Half of the samples contain *Atriplex* sp(p). (oraches), *Carex* sp(p). (sedges), *Centaurea* sp(p). (knapweeds), *Coriandrum sativum* (coriander), *Corylus avellana* (hazel), *Juncus bufonius* (toad rush), *Lapsana communis* (nipplewort), *Prunus domestica* (plum), *Prunus* cf. *domestica* ssp. *insititia* (plum), *Rubus idaeus* (raspberry), *Rumex* sp(p). (docks) and *Sphagnum* sp(p). (*Sphagnum* moss leaves and stem fragments). These samples have a strong "cess pit" flavour with many food remains present, along with faecal concretions.

All but sample 185 contain mineralised remains (4, 1 and 5 taxa are present in samples 32, 58 and 30 respectively); all of the samples with mineralised remains contain fish bone, and mammal bone is also present in samples 58 and 30.

Sample	Deposit type	Date	Total diversity	Plant taxa
305	pit fill	C16th	29	21
306	pit fill	C16th	27	22
36	pit fill	m.-l.C13th	50	40
167	pit fill	C16th	32	27
320	pit fill	C16th	40	36
5	pit fill	?	42	38
235	pit fill	m.C10th-m.C11th	40	36
319	pit fill	m.C10th-m.C11th	52	46
16	?	?	67	61
34	pit fill	m.-l.C14th	71	63
18	pit fill	?	50	46
19	pit fill	?	50	44
7	pit fill	?	40	34
12	pit fill	?	42	36
21	pit fill	?	31	26
22	pit fill	?	33	24
13	pit fill	?	54	45

These 17 samples represent 4 different sites and are pit fills with the exception of sample 16, which is of unknown provenance and may also have originated in a pit. Some of the samples are undated but those which are dated cover a range from the mid 10th to 16th Century. Slightly below average to relatively diverse fossil assemblages were recovered from the samples but only *Agrostemma githago* (corncockle) and *Triticum/Secale* (wheat/rye "bran") are found in all. All but one sample contains *Malus sylvestris* (crab apple), and 15 of them contain faecal concretions and *Rumex* sp(p). (docks). Fourteen samples contain *Atriplex* sp(p). (oraches) and *Linum usitatissimum* (flax); 13 contain eggshell membrane fragments, mammal bone and *Lapsana communis* (nipplewort); 12 contain *Chrysanthemum segetum* (corn marigold), *Rubus fruticosus* (blackberry) and fly puparia; 11 contain fish bone along with *Centaurea* sp(p). (knapweeds), *Sambucus nigra* (elder) and *Urtica urens* (small nettle); and 10 contain Gramineae, *Polygonum aviculare*

(knotgrass), *Carex* sp(p). (sedges), *Chenopodium album* (fat hen), *Eleocharis palustris* (common spike-rush), *Ranunculus* Section *Ranunculus* (buttercups) and *Urtica dioica* (stinging nettle).

Eight of the samples contain a limited mineralised component (ranging from 1 to 6 taxa) and all of these also contain bones (7 of them both fish and mammal bone).

Sample	Deposit type	Date	Total diversity	Plant taxa
161	fill	C11th-C12th	18	13
189	pit fill	?	28	21
170	pit fill	C12th-C13th	16	14
221	pit fill	C10th	28	25

These samples were all recovered from different sites and comprise 3 pit fills and 1 indeterminate fill. The 3 dated samples range in age from the 10th to the 13th Century. The samples contain plant assemblages of below average diversity, of which 3 taxa are common to all, along with faecal concretions: *Agrostemma githago* (corncockle), *Malus sylvestris* (crab apple; 2 samples just endocarp) and *Triticum/Secale* (wheat/rye "bran" fragments). Three samples contain fish bone, fly puparia and *Urtica dioica* (stinging nettle), while half of them contain *Allium* sp(p). (leek/garlic), *Bilderdykia convolvulus* black bindweed), *Prunella vulgaris* (selfheal), *Torillis japonica* (upright hedge parsley), *Ranunculus* Section *Ranunculus* (buttercups), *Rubus fruticosus* (blackberry), mammal bone and eggshell membrane fragments.

B1(iii) Part 3(d)

This sub-cluster comprises just one sample:

Sample	Deposit type	Date	Total diversity	Plant taxa
308	pit fill	C12th	30	27

This pit fill contains a plant assemblage of just below average diversity, with 27 organically preserved plant taxa, along with earthworm egg caps, faecal concretions and *Trichuris* eggs.

B1(iv)

Sample	Deposit type	Date	Total diversity	Plant taxa
27	pit fill	m.C15th-e.C17th	19	12
59	?	?	21	16
52	gully fill	m.-l.C14th	14	12
218	pit fill	C10th	18	13
217	build-up	e.-m.C11th	19	15

These 5 samples represent 4 different sites, and comprise 2 pit fills, a gully fill and a build-up, along with a sample of indeterminate provenance. The samples range from the 10th to early 17th Century. They all contain below average, relatively low diversity fossil assemblages, with only sedges (*Carex* sp(p).) and fly puparia common to all. Four of the samples contain earthworm egg caps, fish bone and the plants *Eleocharis palustris* (common spike-rush) and *Ranunculus* Section *Ranunculus* (buttercups). *Atriplex* sp(p). (oraches), *Bilderdykia convolvulus* black bindweed) and *Rumex acetosella* (sheep's sorrel) are present in 3 of the samples.

Samples 27 and 217 contain one mineralised plant taxon each, along with fish bone. The other samples totally lack mineralised remains.

B1(v)

This sub-cluster comprises just one sample:

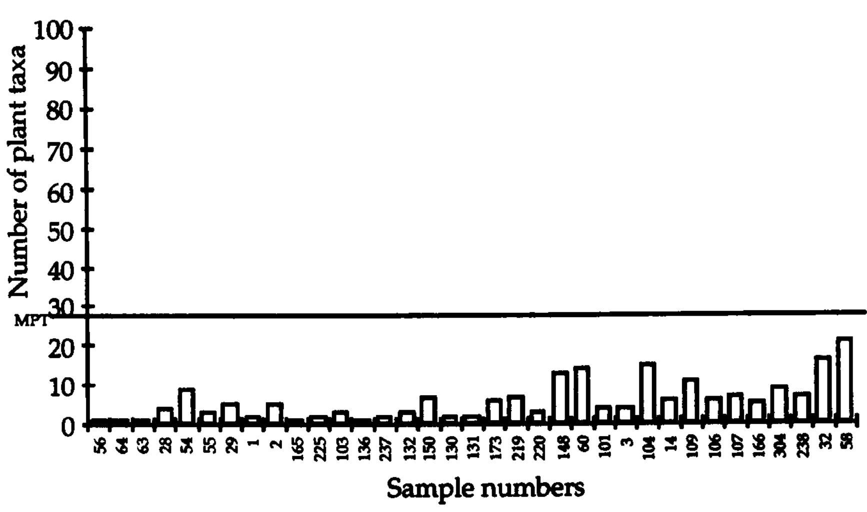
Sample	Deposit type	Date	Total diversity	Plant taxa
195	ditch fill	C15th	28	22

This ditch fill contains a below average diversity fossil assemblage, comprising mineralised *Malva* sp(p). (mallow), along with 21 organically preserved plant taxa, beetles, bone fragments, *Daphnia* ephippia, fish bone, leather fragments and marine mollusc shell fragments.

4. 3. 2. Cluster analysis of contexts (samples) based on taxonomically identified plant remains alone

The results of cluster analysis of the E. A. U. samples based on their contained taxonomically identified plant fossils are presented in Figure 4.6. (foldout dendrogram). One sample forms an out-group to the others in the dendrogram (sample 110 = 81.12/1162; layer; e.C4th), due to the total absence of named plant remains. If this sample is ignored, the remaining samples form a pattern similar to the dendrogram for plant, vertebrate and invertebrate remains (Figure 4. 1), with two major clusters, one (**A**) containing about a fifth of the samples, the other (**B**) accommodating the remainder. The samples occur within the same main cluster as the one they occupy in the dendrogram for all biological remains (Figure 4. 1.), with a few exceptions, but the composition of many of the minor clusters has changed. The site/context codes for each sample are listed in Table 4.1., and the sites corresponding to the codes in Table 4. 2. The deposit type and age of each sample are summarised in tables below, along with the number of plant taxa recovered from each sample. As before, sub-cluster labels correspond to those on the dendrogram. The number of

Figure 4. 6. Dendrogram produced by cluster analysis (using Jaccard Coefficient and average linkage between groups) of archaeological samples in the E. A. U., University of York finds database, based on their contained assemblages of seeds, grains and other propagules.



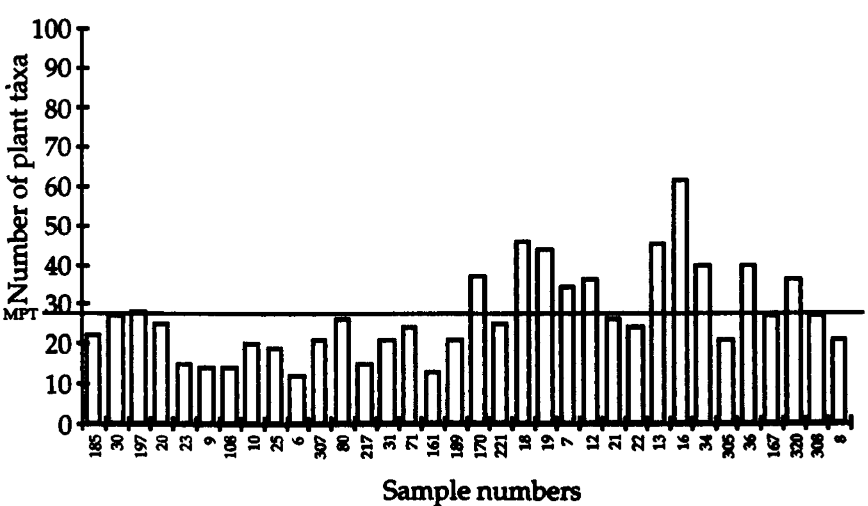


Figure 4. 7. Numbers of plant taxa recovered from the samples processed by the Environmental Archaeology Unit, York which were analysed using cluster analysis. Sample numbers are in the order in which they appear in the dendrogram based on plant remains only (Figure 4. 6.). MPT indicates the mean number of plant taxa recovered per sample (27.5).

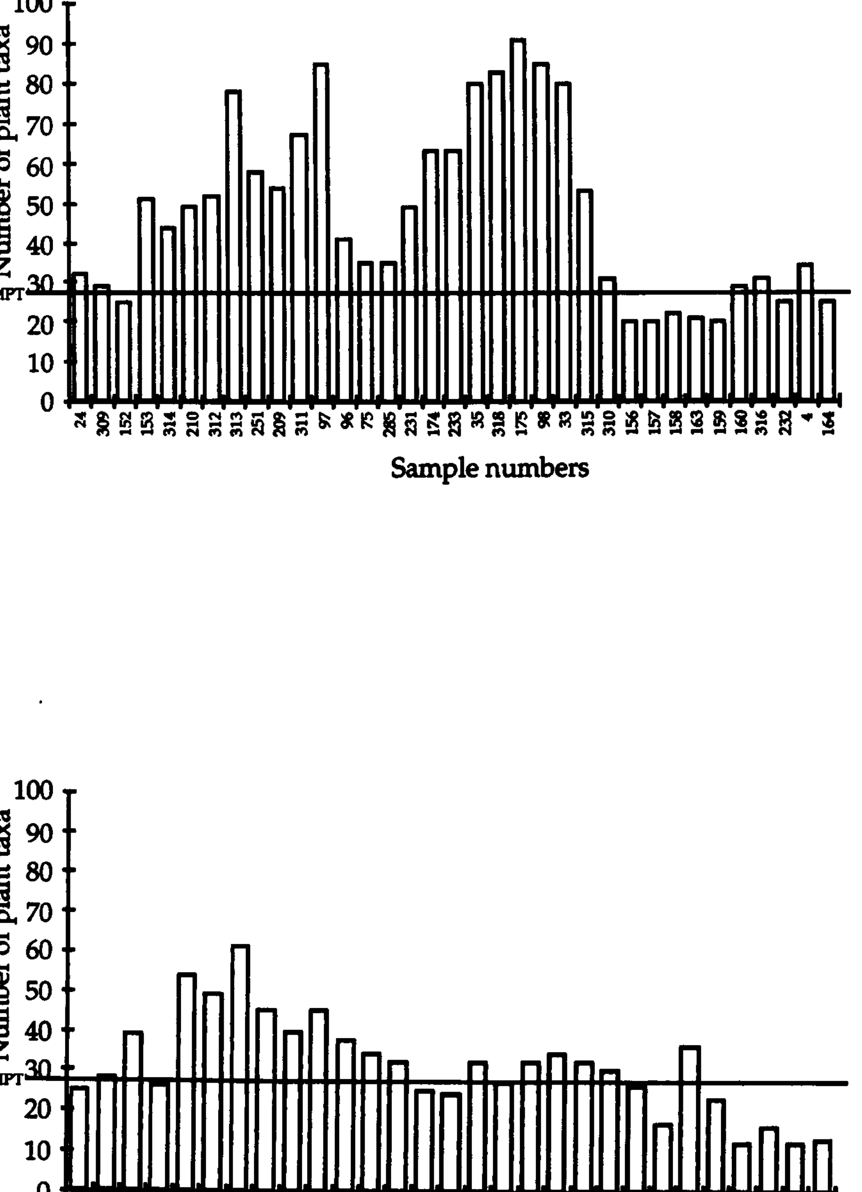


Figure 4. 7. ctd.

plant taxa present in the samples is represented in Figure 4. 7., with the mean number of taxa per sample indicated as a measure of relative diversity.

Cluster A

A(i)(a)

Part One

Sample	Deposit type	Date	Plant taxa
56	pit fill	m.C17th	1
64	occupation layer	m.C15th-e.C17th	1
63	pit fill	m.C15th-e.C17th	1
28	pit fill	m.C15th-e.C17th	4
54	pit fill	l.C14th-e.C15th	9
55	pit fill	l.C14th-e.C15th	3
29	pit fill	m.C15th-e.C17th	5
1	stone-lined pit fill	?	2
2	stone-lined pit fill	?	5

These samples come from three different sites and all but one (an occupation layer) are pit fills. The samples range in age from the late 14th to the early 17th Century. Plant remains are very rare in these samples: some yield just one species (fig: *Ficus carica*). The samples are united by the presence of fig (*Ficus carica*) seeds, and 5 out of 9 samples contain elder (*Sambucus nigra*) seeds. Mineralised remains are present in 6 out of 9 samples. Since pit fills are very unlikely to have contained just fig and elder seeds originally, these samples are interpreted as the robust remains of an originally diverse flora which has been significantly degraded.

Part Two

Sample	Deposit type	Date	Plant taxa
126	bore hole	?Medieval	1
225	pit back fill	C13th-C14th	2
103	timber-lined pit fill	e.C13th	3
136	?fire remains	e.-m.C14th	1
237	pit fill	C12th	2
132	pit fill	C16th-C17th	3
150	pit fill	C13th-C14th	7

These samples represent six different sites and comprise 1 bore hole sample and 6 pit fills. The age of the samples ranges from the 12th to the 17th century. Few plant remains are present in the samples and none is common to all. *Sambucus nigra* (elder) is found in 4 of the 7 samples and *Agrostemma githago* (corncockle) in 3. Mineralised remains are present in 3 of the samples.

A(i)(b)

This sub-cluster contains just two samples, both pit fills from the same site (l.C7th-m.C9th):

Sample	Deposit type	Date	Plant taxa
130	pit fill	l.C7th-m.C9th	2
131	pit fill	l.C7th-m.C9th	2

The samples are united only by the presence of mineralised *Brassica* sp./*Sinapis arvensis* (cabbage, etc./charlock) seeds.

A(i)(c)

The four samples in this sub-cluster represent 3 different sites and include 2 pit fills, 1 post hole fill and 1 barrel well fill. The samples cover a large time span, from Roman times (*ca.* AD 40-400) to the 10th century.

Sample	Deposit type	Date	Plant taxa
173	pit fill	Roman	6
219	barrel well fill	C10th	7
220	pit fill	C10th	3
148	post-hole fill	l.C7th-m.C9th	13

Plant remains are relatively rare and no taxon is found in all samples. *Agrostemma githago* (corncockle) and Cerealia are found in 3 out of 4 samples and *Bilderdykia convolvulus* black bindweed), *Brassica* sp./*Sinapis arvensis* (cabbage, etc./charlock), *Linum usitatissimum* (flax) and *Malus sylvestris* (crab apple; 1 sample contains just endocarp and 1, mineralised seeds) are found in half of the samples. Only half of the samples contain mineralised remains.

A(ii)

Sample	Deposit type	Date	Plant taxa
60	pit fill	l.C14th-e.C15th	14
101	well fill	C13th-C14th	4
3	cess pit?	?	4
104	timber pit lining	e.C13th	15
14	pit fill	?	6
109	pit fill	Anglo-Scandinavian	11
106	timber pit lining	e.C13th	6
107	pit fill	e.C13th	7

These samples are all pit fills, representing 4 sites. The age range is Anglo-Scandinavian (9th to 11th Century) to early 15th Century. No

taxon is common to all, but *Sambucus nigra* (elder) is found in 6 of the 8 samples and *Avena* sp(p). (oats) in 3. Plant remains are relatively rare in all of the samples, and all but 101 contain some mineralised remains.

A(iii)

Sample	Deposit type	Date	Plant taxa
304	?	?	9
166	hollow	late Medieval	5

These samples both contain few plant remains, of which *Reseda luteola* (weld), *Urtica dioica* (stinging nettle) and *Viola* sp(p). (violets/field pansies) are common to both. Neither sample contains any mineralised remains.

A(iv)

This sub-cluster comprises one sample only, which contains 7 organically preserved plant taxa:

Sample	Deposit type	Date	Plant taxa
238	dump	C12th	?

Cluster A Overall

All of the samples in Cluster A contain few plant species, and clusters are usually linked by just one or two common species. In some samples, e. g. the bore hole sample, the impoverished fossil plant assemblage may reflect an originally restricted flora in the context sampled. However, the majority of samples are assumed to represent highly degraded deposits, in which only robust or mineralised taxa survive.

Cluster B

This cluster comprises one tiny cluster (**B(ii)**) and another (**B(i)**), which contains the majority of samples. These are discussed below within their smaller sub-clusters.

B(i)(a)

Sample	Deposit type	Date	Plant taxa
32	floor	e.-m.C14th	16
58	pit fill	l.C14th-e.C15th	21
185	well fill	l.C14th-C16th	22
30	basal pit fill	m.C15th-e.C17th	27
197	?ditch fill	Medieval	28

These 5 samples represent 3 different sites and comprise 2 pit fills, a well fill, a floor deposit and a possible ditch fill. The samples range in age from the middle 14th to 16th Century. The first 4 samples also formed a cluster in the analysis based on all biological remains (Fig. 4. 1.).

The samples typically contain below average diversities of plant taxa, of which only *Ficus carica* (fig) is common to all. In addition, a number of taxa occur in the majority of samples: *Agrostemma githago* (corncockle), *Fragaria vesca* (wild strawberry), *Rubus fruticosus* (blackberry), *Triticum/Secale* ("bran") (wheat/rye "bran") and *Vitis vinifera* (vine/grapes) in 4 samples; and *Atriplex* sp(p). (oraches), *Carex* sp(p). (sedges), *Corylus avellana* (hazel), *Foeniculum vulgare* (fennel), *Prunus domestica* (plum) and *Rubus idaeus* (raspberry) in 3.

Two of the samples contain crab apple endocarp and one contains seed cup bases, whilst the seeds themselves are absent. Since crab apple seeds have a non-lignified composition comprising non-hydrolysable tannins and cellulose (see **Chapter 2**), their absence suggests that the samples are relatively poorly preserved, so that any seeds in the original floral assemblage that lacked lignin have decayed.

Despite the fact that only two of the samples are pit fills, their contained floras give a strong "cess pit" signal: most of the common species represent the remains of fruits and other edible items.

B(i)(b)

Sample	Deposit type	Date	Plant taxa
20	pit fill	?	25
23	?floor	?	15
9	pit fill	?	14
108	pit fill	e.C13th	14
10	pit fill	?	20
25	pit fill	?	19
6	pit fill	?	12
307	pit fill	?C4th	21

These samples represent three sites, with all but one sample (a possible floor deposit) recovered from a pit. The age range is quite large, from the ?C4th to the early 13th Century. The diversity of the samples is below average and all but one contain *Agrostemma githago* (corncockle). In addition, 7 samples contain *Rubus fruticosus* (blackberry) and *Sambucus nigra* (elder); 6 samples yielded *Atriplex* sp(p). (oraches). *Lapsana communis* (nipplewort), *Triticum/Secale* (wheat/rye "bran"), *Urtica dioica* (stinging nettle) and *Urtica urens* (small nettle) were recovered from 5 samples, and 4 samples contain *Centaurea* sp(p). (knapweeds).

B(i)(c)

Sample	Deposit type	Date	Plant taxa
80	?	post-Conquest Medieval (1066-1500)	26
217	build-up	e.-m.C11th	15

These two samples were recovered from different sites and potentially from different types of deposit, although there is some overlap in age. Both samples contain a below average diversity of plants, and they share the following taxa: *Agrostemma githago* (corncockle), *Atriplex* sp(p). (oraches), *Carex* sp(p). (sedges), *Chenopodium murale* (nettle-leaved goosefoot), *Ranunculus sceleratus* (celery-leaved buttercup) and *Stellaria media* (common chickweed). Sample 217 yielded one mineralised taxon but sample 80 does not contain any. The dominance of weed species in the build-up sample is consistent with the input of a significant background "rain" of weed species.

B(i)(d)

Sample	Deposit type	Date	Plant taxa
31	organic layer	l.C14th-e.C15th	21
71	pit in bank	C12th-C14th	24

These two samples are of different types (an organic layer and a pit fill), from different sites and of different ages (although their age ranges overlap in the late 14th Century).

Both samples contain below average plant diversities and they have a number of taxa in common: *Agrostemma githago* (corncockle), *Chenopodium album* (fat hen), *Conium maculatum* (hemlock), *Eriophorum vaginatum* (harestail cotton grass), Leguminosae (legumes), *Ranunculus* Section *Ranunculus* (buttercups), *Scandix pecten-veneris* (shepherd's needle) and *Sphagnum* sp(p). (*Sphagnum* moss). The dominance of weed species in the organic layer is consistent with the contribution of a background "rain" of their seed during its accumulation.

Sample 71 contains one mineralised plant taxon but sample 31 lacks any mineralised remains.

B(i)(e)

The vast majority of samples lie within this sub-cluster, which is made up of several smaller groups of samples.

B(i)(e)1

Sample	Deposit type	Date	Plant taxa
161	fill	C11th-C12th	13
189	pit fill	?	21
170	pit fill	C12th-C13th	37
221	pit fill	C10th	25

These samples are all from different sites and comprise 3 pit fills and one indeterminate fill. They range in age from the 10th to the 13th Century. The diversity of the samples is below to slightly above average. Three taxa are common to all: *Agrostemma githago* (corncockle), *Malus sylvestris* (crab apple; all contain endocarp and 2 also contain seeds) and *Triticum/Secale* (wheat/rye "bran"). In addition, 3 samples contain *Ranunculus* Section *Ranunculus* (buttercups), *Rubus fruticosus* (blackberry) and *Urtica dioica* (stinging nettle). Half of the samples contain *Allium* sp(p). (leek/garlic), *Bilderdykia convolvulus* black bindweed), *Chenopodium album* (fat hen), *Corylus avellana* (hazel), Leguminosae (legumes), *Scorpidium scorpioides* (a moss), *Stellaria media* (common chickweed) and *Torilis japonica* (upright hedge parsley).

B(i)(e)2

Sample	Deposit type	Date	Plant taxa
18	pit fill	?	46
19	pit fill	?	44
7	pit fill	?	34
12	pit fill	?	36
21	pit fill	?	26
22	pit fill	?	24
13	pit fill	?	45

16	?	?	61
34	pit fill	m.-l.C13th	40
305	pit fill	C16th	21
36	pit fill	m.-l.C13th	40
167	pit fill	C16th	27
320	pit fill	C16th	36
308	pit fill	C12th	27

These 14 samples represent 4 different sites and are all pit fills, except sample 16 which is of unknown provenance. The age range is 12th to 16th Century. The diversity of the floral assemblages in the samples ranges from below average to relatively high. All samples contain *Agrostemma githago* (corncockle) and *Triticum/Secale* (wheat/rye "bran"). In addition, 13 samples contain *Malus sylvestris* (crab apple; some just endocarp); 12 yielded *Chrysanthemum segetum* (corn marigold), *Atriplex* sp(p). (oraches) and *Rumex* sp(p). (docks); 11 contain *Urtica urens* (small nettle); 10 contain *Lapsana communis* (nipplewort), *Linum usitatissimum* (flax), *Polygonum aviculare* (knotgrass) and *Carex* sp(p). (sedges); 9 samples contain *Centaurea* sp(p). (knapweeds), *Rubus fruticosus* (blackberry), Gramineae (grasses), *Urtica dioica* (stinging nettle) and *Sambucus nigra* (elder); 8 contain *Ranunculus* Section *Ranunculus* (buttercups), *Brassica rapa* (turnip) and *Reseda luteola* (weld); 7 contain *Chenopodium album* (fat hen), *Eleocharis palustris* (common spike-rush), *Malus* sp(p). (apple), *Polygonum persicaria* (redshank), *Prunus spinosa* (blackthorn) and *Stellaria media* (common chickweed). Six of the samples contain *Corylus avellana* (hazel), *Ficus carica* (fig) and *Vaccinium* sp(p). (bilberry/blueberry).

B(i)(e)3

Sample	Deposit type	Date	Plant taxa
8	pit fill	?	21
24	pit fill	?	32
309	pit fill	Anglo-Scandinavian	29

These samples represent 2 sites and are pit fills of unknown and Anglo-Scandinavian age. The floral assemblages present range from below average to average in diversity, and all 3 samples yield: *Agrostemma githago* (corncockle), *Antitrichia curtipendula* (a moss), *Brassica rapa* (turnip), *Polygonum lapathifolium* (pale persicaria), *Ranunculus* Section *Ranunculus* (buttercups) and *Urtica urens* (small nettles). In addition, 2 out of 3 contain: *Bilderdykia convolvulus* (?black bindweed), *Brassica* sp(p). (cabbages, etc.), *Chenopodium album* (fat hen), *Eurynchium striatum* (a moss), *Hypnum cupressiforme* (a moss), *Isothecium myurum* (a moss), *Lamium* Section *Lamiopsis* (dead nettles), *Lapsana communis* (nipplewort), *Neckera complanata* (a moss), *Polygonum aviculare* (knotgrass), *Polygonum hydropiper* (water pepper), *Prunella vulgaris* (selfheal), *Prunus spinosa* (blackthorn), *Raphanus raphanistrum* (wild radish), *Sonchus asper* (prickly sow-thistle) and *Triticum/Secale* ("bran") (wheat/rye).

B(i)(e)4

Sample	Deposit type	Date	Plant taxa
152	pit fill	?Anglo-Scandinavian	25
153	pit fill	?Anglo-Scandinavian	51
314	pit fill	m.-l.C2nd	44

These 3 samples represent 2 sites, are all pit fills and cover a large age range from 2nd Century to Anglo-Scandinavian (*ca* 9th-11th Century). The samples have 10 taxa in common: *Atriplex* sp(p). (oraches), *Carex* sp(p). (sedges), *Chenopodium* Section *Pseudoblitum* (goosefoots), *Ranunculus* Section *Ranunculus* (buttercups), *Rubus fruticosus* (blackberry), *Rumex* sp(p). (docks), *Sambucus nigra* (elder), *Stellaria media* (common chickweed), *Urtica dioica* (stinging nettle) and *Urtica urens* (small nettle).

Two of the three samples contain: *Anagallis arvensis* (scarlet pimpernel), *Calluna vulgaris* (heather), *Chenopodium polyspermum* (?), *Conium maculatum* (hemlock), *Eleocharis palustris* (common spike-rush), *Hyoscyamus niger* (henbane), Gramineae (grasses), *Montia fontana* ssp. *chondrosperma* (blinks), *Papaver somniferum* (opium poppy), *Polygonum persicaria* (redshank), *Potentilla anserina* (silverweed), *Prunella vulgaris* (selfheal), *Ranunculus sceleratus* (celery-leaved buttercup), *Ranunculus flammula* (lesser spearwort), *Rumex acetosella* (sheep's sorrel) and *Sphagnum* sp(p). (*Sphagnum* moss). The plants linking the samples are dominantly weeds, with few edible species present.

B(i)(e)5

Sample	Deposit types:	Date	Plant taxa
210	yard deposit	ca930-5-ca.975	49
312	pit fill	C10th-C11th	52
313	pit fill	C10th-C11th	78
251	fill in feature in building	c.930-5-c.975	58
209	floor	c.975-e.-m.C11th	54
311	pit fill	C11th	67
97	?	C11th-C13th	85
96	floor	C11th-C12th	41
75	pit fill	C11th	35

285	external layer	m.C9th-e.C10th	35
231	backfill of pit cut	C11th-C12th	49
174	upper fill of u-shaped feature	?C12th-C14th	63
233	?	?	63
35	basal pit fill	m.-l.C13th	80
318	pit fill	l.C12th-e.C13th	83
175	pit fill	?C12th-C14th	91
98	backfill of robbed bedding trench	C11th-C12th	85
33	pit fill	l.C14th-e.C15th	80
315	pit fill	l.C14th	53
310	pit fill	m.-l.C14th	31

These 20 samples encompass several sites, deposit types and ages (10th - 15th Century). All contain above average diversities of plant species and many are very diverse. No one plant taxon is present in all samples, although 19 contain *Agrostemma githago* (corncockle); 18 contain *Carex* sp(p). (sedges) and *Ranunculus* Section *Ranunculus* (buttercup); 17 contain *Chenopodium album* (fat hen) and *Raphanus raphanistrum* (wild radish) and 16 contain *Galeopsis* Subgenus *Galeopsis* (hemp nettles), *Lapsana communis* (nipplewort), *Urtica dioica* (stinging nettle), *Atriplex* sp(p). (oraches), *Polygonum persicaria* (redshank), *Stellaria media* (common chickweed), *Anthemis cotula* (stinking chamomile) and *Urtica urens* (small nettle).

Other common species include: *Linum usitatissimum* (flax), *Malus sylvestris* (crab apple; most contain endocarp only), *Sambucus nigra* (elder) and *Eleocharis palustris* (common spike-rush) in 15 samples; *Polygonum aviculare* (knotgrass), *Bilderdykia convolvulus* (?black bindweed) and *Rumex* sp(p). (docks) in 14 samples; *Brassica rapa* (turnip), *Corylus avellana* (hazel), *Hyoscyamus niger* (henbane), *Triticum/Secale* ("bran") (wheat/rye) and *Hypnum cupressiforme* (a moss) in 13 samples; *Brassica* sp./*Sinapis arvensis* (cabbage, etc./charlock), *Rumex acetosella* (sheep's sorrel), *Spergula arvensis* (corn spurrey) and Gramineae (grasses)

in 12 samples; *Neckera complanata* (a moss), *Juncus bufonius* (toad rush), *Prunella vulgaris* (selfheal), Leguminosae (legumes) and *Polygonum lapathifolium* (pale persicaria) in 11 samples, and *Sonchus asper* (prickly sow-thistle), *Avena* sp(p). (oats) and *Calliergon cuspidatum* (a moss) in 10 samples.

Despite the fact that many of these samples (the pit fills) represent deposits which functioned in food storage or as repositories for human waste materials, the plant species uniting them are dominantly weeds. This implies that, at least in this case, the fossil assemblage that is recovered from an archaeological deposit reflects the wild flora of the surrounding area more strongly than the anthropogenic function of the deposit from which it was recovered. This is likely to result from a combination of factors: (1) many prolific weeds produce vast numbers of small seeds, while edible fruits may contain as little as one seed; (2) different seed species have different preservation potentials, so that relatively decay-resistant species will survive where others decay; and (3) edible species may have been cooked and/or have passed through the human gut, both of which are likely to affect their susceptibility to decay.

B(i)(e)6

Part One

Sample	Deposit type	Date	Plant taxa
156	pit fill	?post-Conquest Medieval	20
157	fill	m.C11th-m.C13th	20
158	fill	m.C11th-m.C13th	22
163	?pit fill	?post-Conquest Medieval	21
159	fill	C11th-C12th	20

All of these samples, except sample 163, were also clustered together in the dendrogram based on all biological remains (Figure 4. 3. 1.). They all originate on the same site and are indeterminate fills and pit fills. The samples date from the 11th to 13th Century and the post-Conquest Medieval period (1066-1500), so that they may overlap in age. The contained floras are of below average diversity, with around 20 named plant taxa per sample. All samples contain *Agrostemma githago* (corncockle), *Atriplex* sp(p). (oraches) and *Reseda luteola* (weld). In addition, 4 samples contain *Brassica rapa* (turnip), *Chenopodium* Section *Pseudoblitum* (oak-leaved/red goosefoot), *Ficus carica* (fig), *Juncus bufonius* (toad rush), *Polygonum persicaria* (redshank) and *Rumex acetosella* (sheep's sorrel) and 3 samples yielded *Carex* sp(p). (sedges), *Ranunculus* Section *Ranunculus* (buttercups), *Sambucus nigra* (elder) and *Silene vulgaris* (bladder campion). Two samples yielded *Chrysanthemum segetum* (corn marigold), *Polygonum aviculare* (knotgrass), *Ranunculus sardous* (hairy buttercup), *Rubus fruticosus* (blackberry), *Rumex* sp(p). (docks), *Silene alba* (white campion) and *Urtica dioica* (stinging nettle).

Part Two

Sample	Deposit type	Date	Plant taxa
160	fill	?	29
316	pit fill	m.C13th-C14th	31
232	dump	C11th-C12th	25

These samples represent 3 different sites, deposit types and ages. The contained floras are of average diversity and the samples have 7 taxa in common: *Agrostemma githago* (corncockle), *Atriplex* sp(p). (oraches), *Chenopodium album* (fat hen), *Eleocharis palustris* (common spike-rush),

Ranunculus sceleratus (celery-leaved buttercup), *Sambucus nigra* (elder) and *Stellaria media* (common chickweed).

In addition, a number of taxa were recovered from 2 of the samples: *Brassica rapa* (turnip), *Brassica* sp./*Sinapis arvensis* (cabbage, etc./charlock), *Corylus avellana* (hazel), Gramineae (grasses), *Hyoscyamus niger* (henbane), *Lamium* section *Lamiopsis* (dead nettles), *Linum usitatissimum* (flax), *Lychnis flos-cuculi* (ragged robin), *Ranunculus* Section *Ranunculus* (buttercups), *Rubus fruticosus* (blackberry), *Rumex acetosella* (sheep's sorrel) and *Urtica urens* (small nettle).

Part Three

Sample	Deposit type	Date	Plant taxa
4	pit fill	?	34
164	?pit fill	?post-conquest Medieval	25
17	?pit/trench fill or floor	?	25

These samples represent 2 sites but the deposit types and ages are incompletely known. The floras contained in the samples are of just below or above average diversity and 5 taxa are present in all 3 samples: *Agrostemma githago* (corncockle), *Eleocharis palustris* (common spike-rush), *Ranunculus* Section *Ranunculus* (buttercups), *Urtica dioica* (stinging nettle) and *Urtica urens* (small nettle).

In addition, a number of other taxa are found in 2 out of the 3 samples: *Aethusa cynapium* (fool's parsley), *Antitrichia curtipendula* (a moss), *Atriplex* sp(p). (oraches), *Brassica rapa* (turnip), *Carex* sp(p). (sedges), Cerealia (cereals), *Corylus avellana* (hazel), *Ficus carica* (fig), *Galeopsis* subgenus *Galeopsis* (hemp nettles), *Juncus bufonius* (toad rush), *Lapsana communis* (nipplewort), *Linum usitatissimum* (flax), *Polygonum*

lapathifolium (pale persicaria), *Ranunculus sardous* (hairy buttercup), *Reseda luteola* (weld) and *Solanum nigrum* (black nightshade).

Part Four

Sample	Deposit type	Date	Plant taxa
61	pit fill	l.C14th-e.C15th	28
62	pit fill	m.C15th-e.C17th	39
65	pit fill	e.-m.C13th	26
48	pit fill	m.-l.C14th	54
50	pit fill	m.-l.C14th	49
37	pit fill	e.C14th	61
49	pit fill	m.-l.C14th	45
227	dump	C12th-C13th	40
317	pit fill	e.-m.C13th	45
234	silt layer	C12th	38
69	bank	C12th-C14th	34
321	pit fill	C14th	32
151	pit fill	C13th-C14th	25

These 13 samples represent 7 sites and, although the majority are pit fills, they also include a bank, a dump and a silt layer. The dates of the samples range from the 12th to the 17th Century. The samples typically contain above average diversity floras of around 30 to 60 named taxa, although none of these occurs in all.

Twelve of the samples yield *Carex* sp(p). (sedges), *Chenopodium album* (fat hen), *Eleocharis palustris* (common spike-rush), *Rumex acetosella* (sheep's sorrel) and *Urtica dioica* (stinging nettle); 11 contain *Agrostemma githago* (corncockle), *Atriplex* sp(p). (oraches), *Sambucus nigra* (elder) and *Stellaria media* (common chickweed); 10 contain *Bilderdykia convolvulus* (?black bindweed), *Chrysanthemum segetum* (corn marigold) and *Ranunculus* Section *Ranunculus* (buttercups); 9 contain *Brassica rapa* (turnip), *Ranunculus flammula* (lesser spearwort), *Raphanus raphanistrum* (wild radish), *Anthemis cotula* (stinking chamomile), *Centaurea* sp(p). (knapweeds), *Juncus bufonius* (toad rush) and

Ranunculus sceleratus (celery-leaved buttercup); 8 contain *Lapsana communis* (nipplewort), *Polygonum persicaria* (redshank), *Polygonum aviculare* (knotgrass), *Reseda luteola* (weld) and *Sphagnum* sp(p). (*Sphagnum* moss); 7 contain *Rumex* sp(p). (docks), *Conium maculatum* (hemlock) and *Triticum/Secale* (wheat/rye "bran"); 6 contain *Corylus avellana* (hazel) and *Urtica urens* (small nettle); 5 contain *Fragaria vesca* (wild strawberry), *Malus sylvestris* (crab apple), *Polygonum hydropiper* (water pepper) and *Spergula arvensis* (corn spurrey) and 4 contain *Papaver argemone* (prickly poppy) and *Rubus fruticosus* (blackberry).

Part Five

Sample	Deposit type	Date	Plant taxa
325	pit fill	Anglo-Scandinavian	24
326	pit fill	Anglo-Scandinavian	32
171	pit fill	Anglo-Scandinavian	27
322	pit fill	Anglo-Scandinavian	32
324	pit fill	Anglo-Scandinavian	34
323	pit fill	Anglo-Scandinavian	32
327	pit fill	Anglo-Scandinavian	30
290	pit fill	l.C9th-c.930-5	26
162	fill	post-conquest Medieval	17

The first 7 samples are from the same site and all but sample 323 form a cluster in the dendrogram based on all biological remains. All samples are of roughly equivalent age (Anglo-Scandinavian: 9th-11th Century), although the post-Conquest Medieval period covers a huge expanse of time from 1066 to 1500 so sample 162 is likely to be younger.

The majority of the samples contain plant assemblages of above average diversity, and all contain *Atriplex* sp(p). (oraches), *Chenopodium album* (fat hen), *Sambucus nigra* (elder), *Urtica dioica* (stinging nettle) and *Urtica urens* (small nettle). In addition, 8 samples contain *Agrostemma githago* (corncockle), *Chenopodium* Section *Pseudoblitum* (goosefoots),

Polygonum aviculare (knotgrass) and *Stellaria media* (common chickweed); 7 contain *Carex* sp(p). (sedges), *Rumex* sp(p). (docks) and *Scorpidium scorpioides* (a moss) and 6 contain *Corylus avellana* (hazel) and *Hyoscyamus niger* (henbane). Five samples contain *Ranunculus flammula* (lesser spearwort).

B(i)(e)7

This sub-cluster contains just one sample:

Sample	Deposit type	Date	Plant taxa
193	oven	C13th	36

These oven remains contain a relatively diverse charred plant assemblage, along with mineralised corncockle seed fragments.

B(i)(f)

Sample	Deposit type	Date	Plant taxa
239	dump	C11th-C12th	23

This sample yielded a below average diversity flora of 23 organically preserved taxa.

B(ii)

Sample	Deposit type	Date	Plant taxa
27	pit fill	m.C15th-e.C17th	12
59	?	?	16
52	gully fill	m.-l.C14th	12
218	pit fill	C10th	13

These samples from 3 different sites yielded fairly restricted, below average diversity floras. Only *Carex* sp(p). (sedges) is common to all samples, although 3 of them contain *Bilderdykia convolvulus* (black bindweed) and *Ranunculus* Section *Ranunculus* (buttercups) and 2 contain *Aethusa cynapium* (fool's parsley), *Atriplex* sp(p). (oraches), *Eleocharis palustris* (common spike-rush), Gramineae (grasses), *Juncus bufonius* (toad rush), *Potentilla* sp(p). (cinquefoils), *Rumex* sp(p). (docks) and *Rumex acetosella* (sheep's sorrel).

4. 3. 3. Cluster analysis of common seeds and grains

The dendrogram (fold-out Figure 4. 8.) comprises 6 major clusters (A to F). The vast majority of taxa fall within Cluster A, which comprises a number of small sub-clusters, which group to form increasingly large clusters. The results are presented below in the form of lists of the taxa in each (sub-) cluster, in the order that they appear on the dendrogram. Where a number of sub-clusters group together to form a larger cluster, the individual sub-clusters are discussed in turn, before considering what links all members of the cluster. To establish whether the taxa in the clusters are preserved together due to similar ecological preferences or because they were brought onto habitation sites for the same purpose, the provenance of each taxon is considered in turn, and its range of known modern habitats and human uses summarised in a table (Appendix 5). In Appendix 6, the plant communities in which each species is found in modern-day Britain are summarised, according to their listing in Rodwell's British Plant Communities (1991-2000), in order to aid ecological interpretation of the clusters. This five volume work catalogues the results of a 25 year survey of all plant communities found growing in mainland Britain. In the "Modern plant communities"

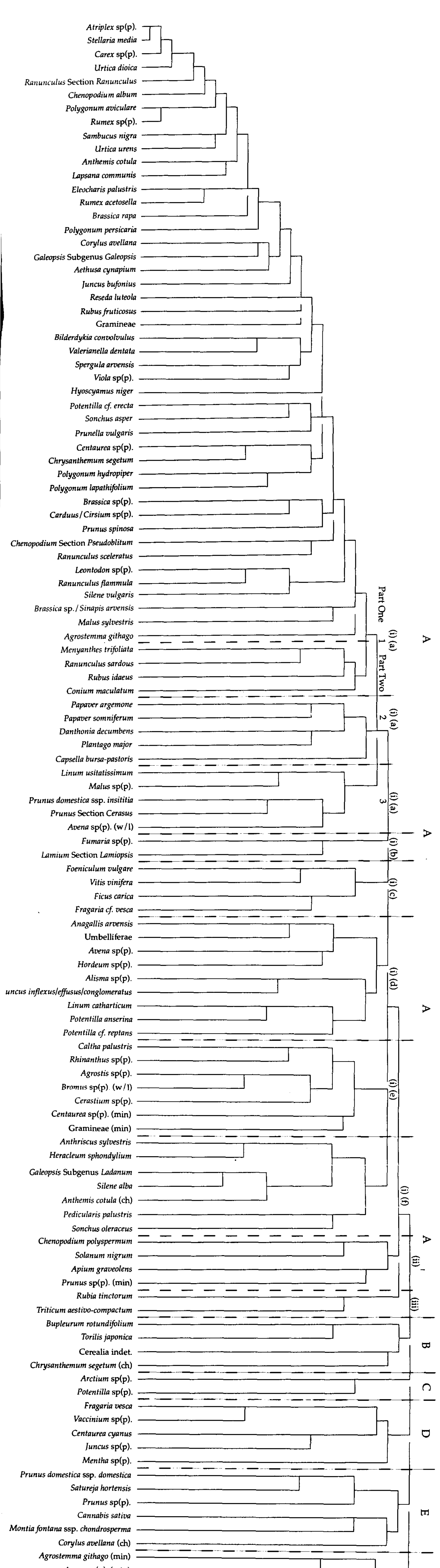


Figure 4. 8. Dendrogram produced by cluster analysis (using Jaccard Coefficient and the average linkage between groups) of common (>5 occurrences) seeds and grains in the E. A. U., University of York, database, based on the samples in which they occur.

section of the tables, numbers in bold refer to the volumes of Rodwell (where **1** covers woodlands and scrub, **2** covers mires and heaths, **3** covers grasslands and montane communities, **4** covers aquatic communities, swamps and tall-herb fens, and **5** covers maritime communities and vegetation of open habitats), and the letters and numbers following them in brackets are the codes for the individual plant communities. A full list of the plant communities referred to in the tables may be found in Appendix 6. The general habitat preferences of taxa that are not treated in Rodwell were determined from Stace's (1997) "New Flora of the British Isles".

A (i) (a) 1 Part One

This sub-cluster contains the largest number of taxa (48), and some of these group together to form smaller, discrete sub-clusters.

Atriplex sp(p). = oraches

Stellaria media = common chickweed

Carex sp(p). = sedges

Urtica dioica = common nettle

Ranunculus Section *Ranunculus* = buttercups

Chenopodium album = fat hen

Polygonum aviculare = knotgrass

Rumex sp(p). = docks

Sambucus nigra = elder

Urtica urens = small nettle

Anthemis cotula = stinking chamomile

Lapsana communis = nipplewort

The twelve taxa above group together to form the smallest scale sub-cluster within Cluster A. These are prolific, common weeds, adaptable to

a range of habitats. Although no one modern plant community contains all of the taxa, individual pairs of taxa are often common to many communities, including some from woodlands, and from a variety of cultivated or otherwise disturbed habitats that would likely occur on and around human habitation sites.

Eleocharis palustris = common spike-rush
Rumex acetosella = sheep's sorrel
Brassica rapa = turnip
Polygonum persicaria = redshank

The four taxa above are not found together in any modern plant communities. However, both *Rumex acetosella* and *Polygonum persicaria* may be found as weeds of disturbed and arable ground, so may have grown on or around human habitation sites, or been brought on-site along with the turnips. *Eleocharis palustris* and *Polygonum persicaria* may be found growing together in marshy habitats.

Corylus avellana = hazel
Galeopsis Subgenus *Galeopsis* = hemp nettles
Aethusa cynapium = fool's parsley

The three taxa above form a sub-cluster but are not found together in any modern plant communities. The hazelnuts are likely to have been brought on-site for consumption, and the hemp nettles may have been found in the same woodland setting, although it seems unlikely that they would be gathered along with nuts. The fool's parsley has nothing in common with the other taxa, and the modern plant communities in which it is recorded in Rodwell are all restricted to the south-east of England so have limited application to interpreting the Yorkshire archaeological plant finds. Hall (2001, *pers comm.*) states that hemp

nettles were probably found growing as arable weeds, so may have made it onto human habitation sites as crop contaminants.

Juncus bufonius = toad rush

Reseda luteola = weld

Rubus fruticosus = bramble

Gramineae = indeterminate grasses

The four taxa above cluster with all of the taxa discussed so far but there are no modern plant communities common to all. Individual taxa generally share habitats with some of the other taxa in the cluster, generally in woodlands or open disturbed land. Some species were clearly brought on-site as food items.

Bilderdykia convolvulus = black bindweed

Valerianella dentata = narrow-fruited cornsalad

Spergula arvensis = corn spurrey

Viola sp(p). = violets/field pansies

The four taxa above are not found together in any modern plant communities, although *Bilderdykia convolvulus, Spergula arvensis* and *Viola* sp(p). are found together as part of various cultivated or disturbed ground weed assemblages, and so may have grown on or around human habitation sites. The two modern plant communities in which *Valerianella* has been recorded are geographically restricted to the south-east of England. However, *Bilderdykia convolvulus* and *Viola* sp(p). may also be found in one or more of these south-eastern communities, so it is possible that these three plants grew together in the past.

Hyoscyamus niger = henbane

Potentilla cf. *erecta* = ?tormentil

Sonchus asper = prickly sow-thistle

Prunella vulgaris = selfheal

Tormentil, prickly sow-thistle and selfheal form a discrete cluster in the dendrogram. No one modern plant community contains all three taxa; tormentil and prickly sow-thistle are never recorded together. However, *Potentilla erecta* and *Prunella vulgaris* may be found together in a wide range of habitats (woodland, coastal, mire and grassland). Prickly sow-thistle may be found along with selfheal in ungrazed grassland and along trampled trackways and, although tormentil has not been recorded in the same community in modern-day Britain, it has been found in a different trampled trackway community, so that it may have grown with the other two species in the past.

Centaurea sp(p). = knapweeds

Chrysanthemum segetum = corn marigold

Polygonum hydropiper = water pepper

Polygonum lapathifolium = pale persicaria

The four taxa above form a sub-cluster in the dendrogram but all are not found together in any modern plant communities. *Centaurea* sp(p). may be found with *Polygonum hydropiper* in lowland mires, but neither species grows along with the other two in the cluster. *Chrysanthemum segetum* and *Polygonum persicaria* may be found growing together as weeds in crop fields, so they may have been brought onto human habitation sites as crop contaminants. Hence, it is likely that at least two different plant communities are represented by the taxa in this cluster.

Brassica sp(p). = indeterminate members of the cabbage family

Carduus/Cirsium sp(p). = thistles

Prunus spinosa = blackthorn

The three taxa above form a discrete sub-cluster in the dendrogram. The *Brassicas* are likely to have been brought on-site as food items, and the thistles and blackthorn may be found growing together in various woodland habitats.

Chenopodium Section *Pseudoblitum* = goosefoots
Ranunculus sceleratus = celery-leaved buttercup

The two taxa above form a discrete couplet in the dendrogram, and in modern-day Britain have been recorded together only in 4: S20, a moist brackish salt-marsh community that seems unlikely to be represented in the environments sampled by the York archaeological plant assemblages. However, Hall (2001, *pers comm.*) states that these two taxa may also be found growing together on the drying mud at pond edges.

Leontodon sp(p). = hawkbits
Ranunculus flammula = lesser spearwort
Silene vulgaris = bladder campion

The three taxa above form a sub-cluster in the dendrogram, but they are not found together in any modern plant communities. Hawkbits and lesser spearwort are found together in a number of damp habitats, including mires, fens, springs and maritime grasslands and dune-slacks. Bladder campion does not occur in any modern community with lesser spearwort but is found in one frequently inundated grassland community 3: MG11 along with hawkbits.

Brassica sp./*Sinapis arvensis* = cabbage/mustard, etc.
Malus sylvestris = crab apple

Brassica sp./*Sinapis arvensis* and *Malus sylvestris* form a discrete couplet in the dendrogram and both are likely to have been brought onto

human habitation sites as food items, resulting in their deposition together in cess pits and other waste repositories.

Agrostemma githago = corncockle

This species forms an out-group to the other taxa in A(i)(a) 1 Part One, and, although now virtually extinct, in the past it occurred as a common crop contaminant.

A (i) (a) 1 Part One overall

This sub-cluster contains a number of weed taxa from a variety of habitats, along with some species that are assumed to have been brought onto human habitation sites for consumption. Many of the species present are known as prolific weeds that occur almost universally in a variety of disturbed habitats, and these are likely to make up the bulk of the "background rain" of seeds into archaeological deposits. Even within the smallest sub-clusters, the seed taxa can rarely all be attributed to the same modern plant communities, and a wide variety of habitats is needed to accommodate all of those within **A (i) (a) 1 Part One**. It is clear that the plant taxa found together within a deposit may have a number of different sources, and are likely to comprise a mixture of "background" weeds growing on and around an occupation site, weeds from slightly further afield, and plants intentionally introduced through human activities.

A (i) (a) 1 Part Two

Menyanthes trifoliata = bogbean

Ranunculus sardous = hairy buttercup

Rubus idaeus = raspberry

Conium maculatum = hemlock

The raspberries were presumably brought onto ancient habitation sites for consumption, while the other species are weeds. No two species in this cluster are found together in any modern plant communities. However, although there are no reports of *Ranunculus sardous* in Rodwell, it may have been found in the same cultivated/disturbed habitats in which hemlock is found today.

A (i) (a) 2

Papaver argemone = prickly-headed poppy

Papaver somniferum = opium poppy

Danthonia decumbens = heath grass

Plantago major = greater plantain

Capsella bursa-pastoris = shepherd's purse

No modern plant community contains all these taxa. No ecological data are available for the now illegal opium poppy *Papaver somniferum* but its habitat preferences are presumably similar to those of its close relative *Papaver argemone.* The prickly poppy may be found along with shepherd's purse as a weed of dry lowland cereal fields, so both species may have found their way onto human habitation sites as crop contaminants. *Danthonia decumbens* and *Plantago major* are found together today only in two communities from unusual settings, a maritime dune-slack and an oolitic limestone grassland, both of which seem unlikely sources for the York plant assemblages, suggesting that the co-occurrence of these two species in the fossil assemblages is coincidental.

A (i) (a) 3

Linum usitatissimum = flax

Malus sp(p). = apples

Prunus domestica ssp. *insititia* = bullace/damson

Prunus section *cerasus* = dwarf cherry

Avena sp(p). (w/l) = oats (waterlogged)

All of these taxa are food items, which were presumably brought on-site for consumption.

A (i) (b)

Fumaria sp(p). = fumitory

Lamium Section *Lamiopsis* = dead nettles

These two taxa are found together in a number of cultivated or disturbed ground habitats in modern-day Britain, so are likely to have thrived on or around ancient human habitation sites.

A (i) (c)

Foeniculum vulgare = fennel

Vitis vinifera = vine (grapes)

Ficus carica = fig

Fragaria cf. *vesca* = wild (?) strawberry

These are all edible taxa, presumably brought on-site for consumption, leading to their deposition together in cess pits or other organic waste repositories.

A (i) (d)

Anagallis arvensis = scarlet pimpernel

Umbelliferae = indeterminate members of the carrot family

Avena sp(p). = charred oats

Hordeum sp(p). = charred barley

Alisma sp(p). = water plantain

Juncus inflexus/effusus/conglomeratus = hard/soft/compact rushes

Linum catharticum = fairy flax

Potentilla anserina = silverweed

Potentilla cf. *reptans* = creeping (?) cinquefoil

The taxa in this sub-cluster comprise two cereals and a number of weed species. No modern community contains all of the weeds, although the rushes, fairy flax, silverweed and cinquefoil occur together in two modern damp habitat communities (a peat and a coastal dune-slack), and water plantain is also associated with wet places. Scarlet pimpernel is a weed of arable fields, so may have been brought on-site as a contaminant of the cereals. Hence, at least two main sources can be recognised for the taxa in this sub-cluster, a damp habitat and an arable field.

A (i) (e)

Caltha palustris = marsh marigold

Rhinanthus sp(p). = yellow rattle

Agrostis sp(p). = bents

Bromus sp(p). (w/l) = bromes (waterlogged)

Cerastium sp(p). = mouse-ears

Centaurea sp(p). (min) = knapweeds (mineralised)

Gramineae (min) = indeterminate members of the grass family (mineralised)

The habitat range of the grass family is too wide to be usefully compared to the other taxa in this sub-cluster. No modern plant communities include all the other 6 taxa but 5 out of 6 may be found in **2:** M22 a peat/mineral soil community restricted to southern Britain, **3:** MG3 a sub-montane hay meadow, **3:** MG4 seasonally flooded hay meadow, **3:** MG8 periodically flooded pasture and **5:** SD17 a dune-slack community. Whilst some of these habitats are unusual, they all imply a periodically damp setting.

A (i) (f)

Anthriscus sylvestris = cow parsley

Heracleum sphondylium = hogweed

Galeopsis subgenus *ladanum* = broad-leaved hemp nettle

Silene alba = white campion

Anthemis cotula = stinking chamomile

Pedicularis palustris = marsh lousewort

Soncus oleraceus = smooth sow-thistle

No modern plant communities include all the weeds in this sub-cluster. Marsh lousewort is not found along with any of the other taxa today, and is associated with fens, heaths and other damp habitats. Four out of the other five species are found in 5: OV19, an ephemeral plant community found in disturbed verges along trackways. Three out of five are found in a variety of other cultivated and disturbed habitats, consistent with a distribution on or around human habitation sites.

A (ii)

Rubia tinctorum = madder

Triticum aestivo-compactum = wheat (charred)

These species comprise a plant used in dyeing and a cereal crop, both presumably brought on-site for human use.

B

Bupleurum rotundifolium = thorow-wax

Torilis japonica = upright hedge parsley

Cerealia indet. = indeterminate cereals (charred)

Chrysanthemum segetum (ch.) = corn marigold (charred)

The four taxa in this sub-cluster do not appear to have a common provenance. The cereals were presumably brought onto the site

intentionally for consumption, and, as a weed of cultivated and disturbed ground, the corn marigold may have been brought with it as a contaminant. The thorow-wax is now extinct in Britain but was a common weed of corn fields in the past, so may also have been a contaminant of the cereals. In modern-day Britain, the upright hedge parsley is associated with scrub, salt-marsh, sand dune, coastal grassland and disturbed ground habitats, the last suggesting that it may have grown on or around human habitation sites in the past.

C

Arctium sp(p). = burdock

Potentilla sp(p). = cinquefoils

The two taxa in this sub-cluster occur together in a number of modern communities associated with nutrient-rich, disturbed soil, so are likely to have grown on or around ancient human occupation sites.

D

Fragaria vesca = strawberry

Vaccinium sp(p). = bilberry/blueberry

Centaurea cyanus = cornflower

Juncus sp(p). = rushes

Mentha sp(p). = mint

The two fruits (and the mint?) were presumably brought on-site for human consumption. There are no entries for the now extremely rare *Centaurea cyanus* in Rodwell, but it is generally found as a weed in cereal fields, so may have found its way onto human habitation sites as a crop contaminant. Rushes have a large number of modern plant communities in common with mint. Both may have been growing wild in a damp

habitat near the human occupation sites or the rushes may have been brought on-site as a contaminant of the mint.

E

Prunus domestica ssp. *domestica* = plum

Satureja hortensis = summer savory

Prunus sp(p). = plum/sloe/cherry, etc.

Cannabis sativa = hemp

Montia fontana ssp. *chondrosperma* = blinks

Corylus avellana (ch.) = hazel (charred)

There are no entries for summer savory in Rodwell or Stace. However, it is used as a herb so may have been brought on-site for consumption. Blinks are found in damp habitats such as mires and heaths. The other taxa were presumably brought onto occupation sites for human use.

F

Agrostemma githago (min) = corncockle (mineralised)

Avena sp(p). (min) = oats (mineralised)

Pisum sp(p). (min) = peas (mineralised)

These taxa comprise two food items brought on-site for consumption and a common crop contaminant. The fact that these three taxa are mineralised may indicate a similar susceptibility to phosphatisation.

4. 3. 4. The structures and taxa most commonly mineralised in the E.A.U. samples

The most common mineralised structures recovered from the E. A. U. samples analysed in this chapter are faecal concretions which, with over two hundred recorded occurrences, outnumber other mineralised remains tenfold. The graph (Figure 4. 9.) of the "top 30" mineralised

remains overall omits faecal concretions except for those which are very decayed (which are listed separately in the E. A. U. database), rodent droppings and dog coprolites, emphasising the susceptibility of faecal material to phosphatisation. This presumably reflects the presence of bacteria and associated with easily-decayed organic material that can act as an ion source. The other common non-botanical mineralised remains comprise fly puparia, maggots and earthworm egg capsules. The maggots represent early mineralisation of relatively labile tissues, whereas the more robust puparia, egg capsules and wood were presumably either infilled by minerals at a very early stage or persisted in the sediment until conditions favouring phosphatisation developed.

Graph 4. 10. shows the most common mineralised plant remains recovered from all samples processed by the E.A.U. which yielded mineralised remains. The graph includes a number of multiple occurrences of the same or closely related taxa, providing strong evidence that these are particularly susceptible to mineralisation. The most commonly occurring mineralised plant remain, *Prunus* sp(p). stones, has two entries (one comprising uncertain assignments of material to this taxon). The robustness of these structures suggests that the conditions required for phosphatisation usually develop at an advanced stage in the degradation of the organic material in a deposit, when only the most recalcitrant structures remain and are beginning to decay significantly. Both the legumes (indeterminate Leguminosae, *Vicia faba* and *Pisum* sp(p).) and the cereals/grasses (*Avena* sp(p). and indeterminate cereals and grasses) are well represented, suggesting a higher phosphatisation potential for these groups. This is in agreement with previous observations by archaeobotanists. Körber-Gröhne (1991) observed that legumes with "soft seed coats" are often poorly preserved, and this apparent susceptibility to decay would enhance the likelihood of their

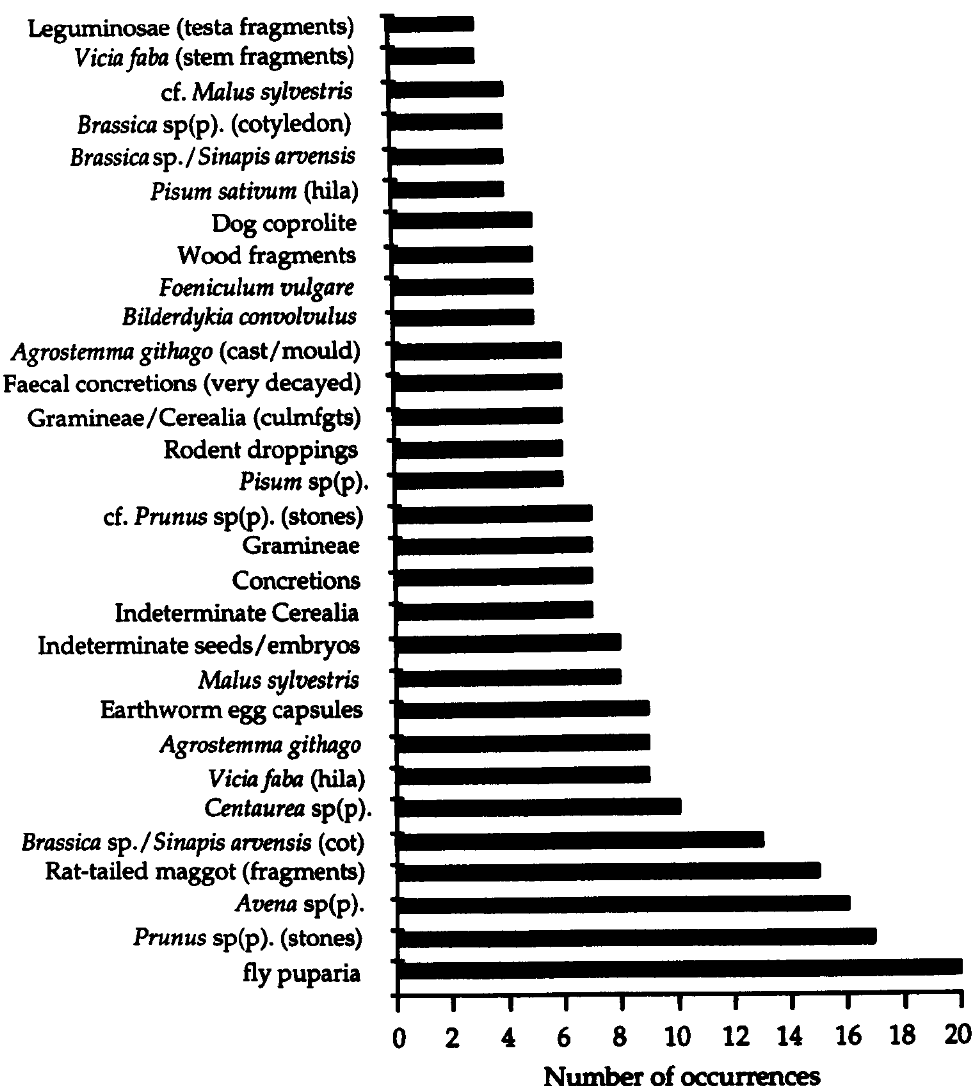


Figure 4. 9. The thirty mineralised biological structures most commonly recorded in the samples from the Environmental Archaeology Unit, University of York analysed using cluster analysis. Plant taxa are represented by seeds, unless otherwise stated. Mineralised faecal concretions were omitted from the graph; occurrences of these outnumber those of other mineralised remains tenfold.
Abbreviations: fgts = fragments, cot = cotyledons.

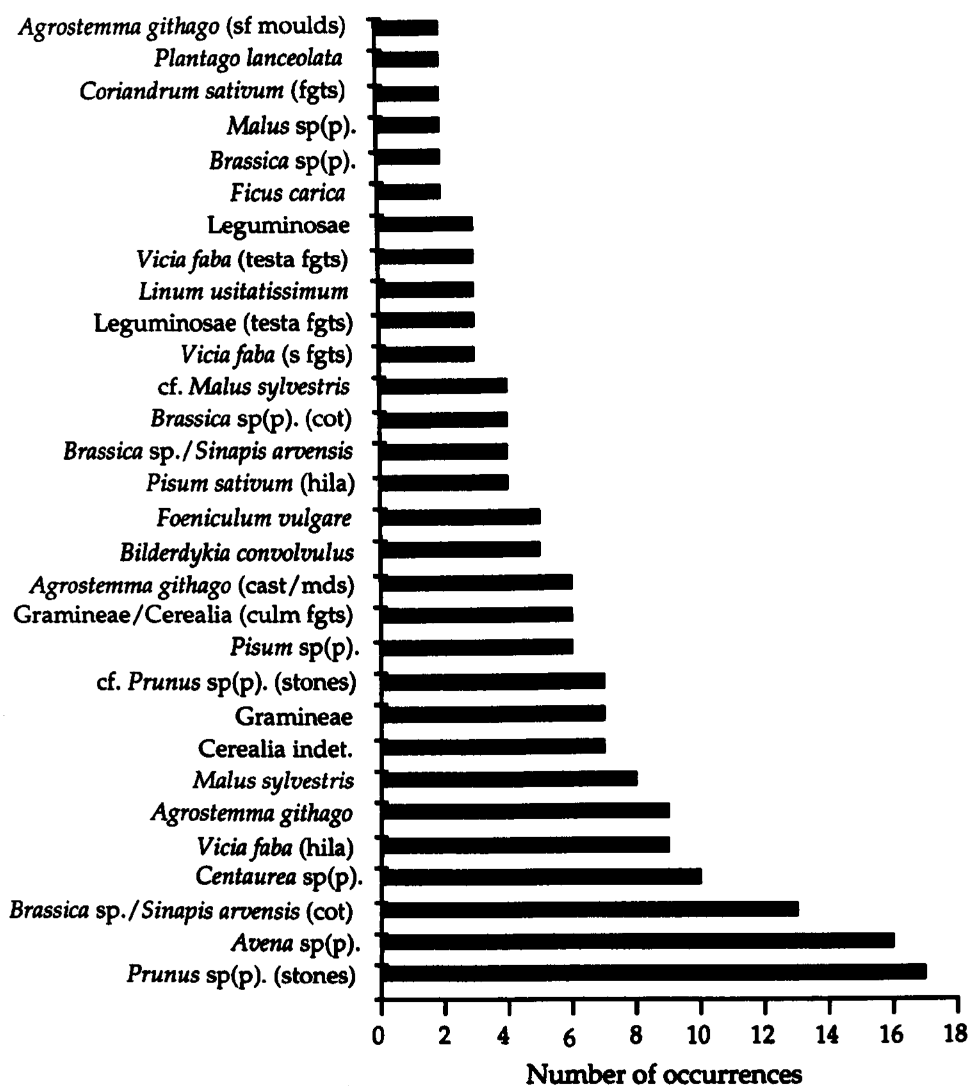


Figure 4. 10. The thirty mineralised plant remains most commonly recorded in the samples from the Environmental Archaeology Unit, University of York analysed using cluster analysis. All taxa are represented by mineralised seeds, unless otherwise stated. Abbreviations: fgts = fragments, cot = cotyledons, s = stem, sf = seed fragments.

mineral replacement. The *Brassicas* have the highest number of entries on the graph. This is consistent with the observation that seeds of these taxa are often found in a poorly preserved state (Greig, 1981), and their low decay resistance makes them more susceptible to mineral replacement. Crab apple seeds are represented three times, which is in agreement with the presence of these seeds as the only mineralised remains in the Coppergate sample studied in Chapter 2. Selective mineralisation of the crab apple seed embryos was attributed to the semi-permeable nature of their seed coats, which allowed the accumulation of ions within them as they decayed. The three entries for corncockle seeds and their mineralised casts and moulds are unsurprising, as the common occurrence of these seed fragments within faecal concretions enhances the likelihood of their phosphatisation by surrounding them with abundant bacteria and an ion source (easily decayed organics).

4. 4. Discussion

4. 4. 1. Cluster analysis of contexts

The cluster analysis of the E. A. U. contexts based on their contained fossil assemblages reveals a number of trends in the nature of fossilisation in archaeological deposits. Seven major conclusions can be drawn on the basis of the results, and the evidence is considered below. Possible interpretations are offered and the means by which they may be tested in the future are outlined.

4. 4. 1. 1. There is a correlation between high rates of decay, taphonomic loss and mineralisation

A high proportion (22 out of 31: 71%) of samples in **Cluster A** of the dendrogram for all biological remains combine very impoverished, well below average diversity fossil assemblages with preservation by

mineralisation. A smaller proportion (40 out of 108: 37%) of the samples in **Cluster B**, which contain much more diverse fossil assemblages (Figures 4. 2. & 4. 4.), yielded mineralised remains. The number of mineralised taxa per sample ranges from 1 to 14 in **Cluster A**, with a mean of 3.32, while **Cluster B** samples yielded between 1 and 7 mineralised remains each, with a mean of 2.05. The difference between the mineralised contents of samples within the two clusters is more marked if the number of mineralised taxa per sample is expressed as a percentage of the overall fossil diversity (i. e. number of different taxa) of the samples. In **Cluster A**, this ranges from 7% to 78%, with a mean of 31%. **Cluster B** samples contain a much smaller proportion of mineralised remains, ranging from 1 to 22%, with a mean of just 5%. The same observations hold for the dendrogram based only on plant remains. Fifty-eight percent of the samples in **Cluster A** (19 out of 33) contain mineralised remains (with diversity ranging from 1 to 11 mineralised taxa per sample), compared to just 36% of samples in **Cluster B** (36 out of 100 samples), which contain between 1 and 6 mineralised taxa each. Considering just those samples that contain some mineralised remains, **Cluster A** samples contain a mean of 2.79 mineralised taxa per sample, as opposed to 1.92 per sample for samples in **Cluster B**. Expressed as percentages of the overall diversity of plant taxa present, **Cluster A** samples contain between 9 and 100% mineralised taxa with a mean of 53%, while samples in **Cluster B** contain between 1 and 25% mineralised taxa, with a mean of just 7% mineralised remains per sample.

It is well established that mineralisation requires a balance between organic decay and replication of tissues by precipitating minerals. It is assumed that the majority of samples yielding very limited diversity have undergone much more degradation than those with very diverse fossil assemblages. The significant decay in the former is more likely to

generate groundwater ion concentrations high enough to allow mineralisation than well-preserved samples where little decay has taken place. Elemental analysis of modern and fossil crab apple pips from Coppergate (**Chapter 2**) revealed that much higher concentrations of phosphorus are required to replace the pips with calcium phosphate than is actually present in modern apple pips. An extra source of phosphorus must be present to allow phosphatisation of plant remains, and in archaeological deposits it is assumed that this is provided by degradation of other organic remains present.

Based on these data, it might be predicted that there would be a negative correlation between total fossil diversity of samples and the number of mineralised taxa that they contain. However, if total diversity is plotted against number of mineralised taxa present (Figure 4. 11.), this result is not obtained. Although the samples yielding the highest numbers of mineralised taxa also contain relatively low overall fossil diversities, the majority of samples are crowded together at the low end of the graph, due to the fact that most samples contain relatively few mineralised taxa, regardless of their overall fossil diversity. Calculation of a correlation coefficient for these data confirms that there is no significant correlation between total fossil diversity and number of mineralised taxa present. The presence of low diversities of mineralised taxa in both low and high diversity fossil assemblages may be due to the mineralised taxa lying at opposing ends of the decay resistance spectrum. Samples preserving very diverse assemblages are likely to represent deposits in which the decay rate was very low, and the majority of taxa present were too decay resistant to degrade and allow their mineralisation. Hence, only relatively easily degraded taxa in these deposits are phosphatised. Conversely, in very degraded deposits, easily degraded taxa may have

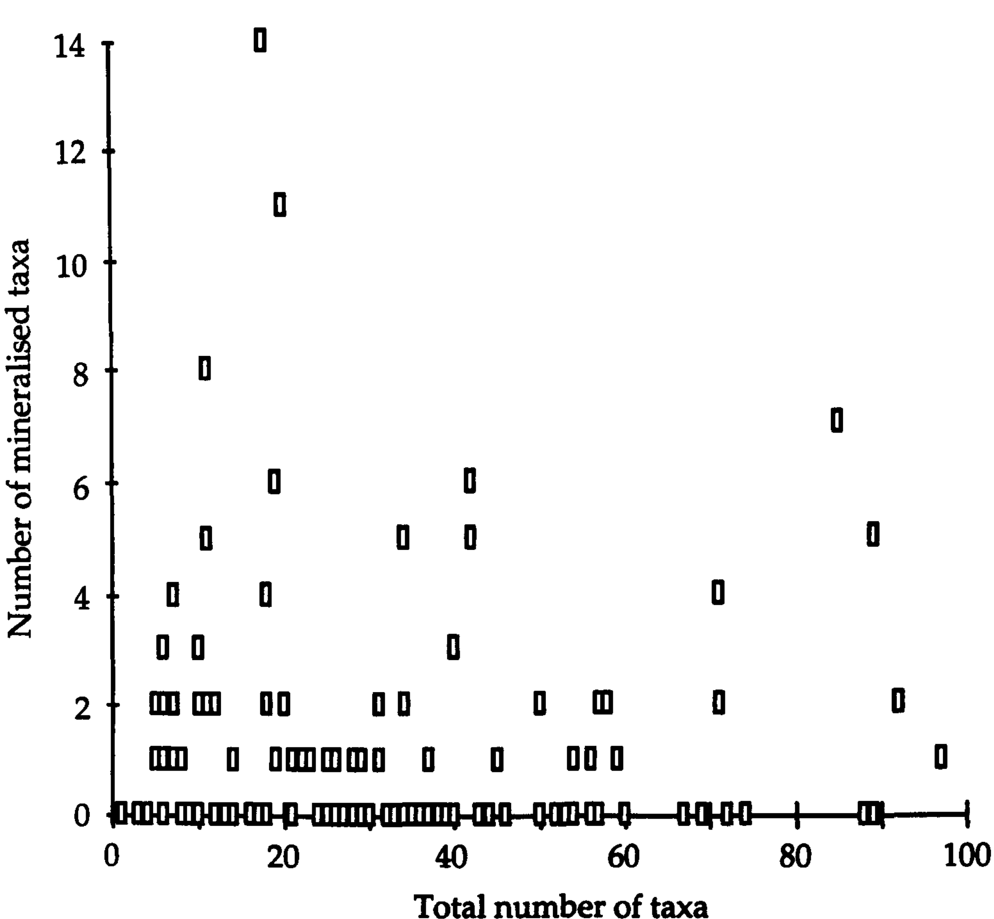


Figure 4. 11. Number of mineralised taxa plotted against total number of fossil taxa recovered from samples processed by the Environmental Archaeology Unit, University of York, which were analysed using cluster analysis.

totally disappeared before the conditions required for phosphatisation develop, so that more decay-resistant taxa are mineralised.

4. 4. 1. 2. There is a correlation between mineralisation and the presence of (fish?) bone

It has been suggested that the presence of fish bone is necessary for mineralisation of organic remains in archaeological deposits and this study supports this hypothesis. Out of 62 samples containing mineralised remains in the dendrogram based on all biological remains (Figure 4. 1.), 56 (90%) also yield fish bones, and 45 (73%) contain mammal bone. Only one sample yielding mineralised fossils (10 = 73-5.14/1758T; pit fill; ?) did not contain bones. The strong correlation between the presence of bones and mineralised remains may be explained in one of two ways. Firstly, bones may be necessary for phosphatisation, perhaps as a calcium or phosphorus source. This idea contradicts the results of XRD analysis carried out on bones from cess pits at St. Saviourgate (**Chapter 2**), which revealed minimal alteration of the mineral portion of the bones, suggesting that they did not contribute significantly to the ions that had affected phosphatisation of faecal concretions and organic remains in the pits.

A second explanation is that bones are more likely to survive in conditions that favour phosphatisation. In (at least periodically) waterlogged deposits such as cess pits, where there is reduced through-flow of water, bone mineral alteration (including dissolution that would free ions for phosphatisation) is likely to occur mainly through the diffusion of ions into the groundwater along concentration gradients (Hedges *et al.*, 1995). In deposits where phosphatisation is favoured, concentrations of groundwater calcium and phosphorus ions are very high, so there is no concentration gradient along which these ions can

diffuse away from bones. Hence, any bones present in the deposit are likely to remain relatively unaltered.

The presence of a sample which contains mineralised remains but no bones appears to contradict both explanations, since bones were apparently neither present to supply the ions for phosphatisation (unless they have completely solubilised), nor did they persist along with the mineralised remains. One possible explanation is that bones were not originally present in the sample and are not required for phosphatisation at all. Alternatively, the ions that affected phosphatisation in this sample may have originated in organic matter other than bones or in bones at different levels in the pit, which were transported in groundwater to the sites of mineralisation.

The dominance of fish bone over the remains of the other vertebrates may reflect the importance of fish in ancient diet or may simply be a result of the small size of the bones, making them more likely to be deposited in cess pits in large numbers. The larger bones of mammals are more likely to have been carried off by dogs, so that they do not become deposited in refuse or cess pits on human habitation sites. Although small fish bones are quite soft if they have been cooked, and might therefore be expected to alter more easily than mammal bones, XRD analysis (**Chapter 2**) revealed no difference in the extent of hydroxyapatite alteration of the two groups of bones.

4. 4. 1. 3. Certain types of seeds are more decay resistant than others

Although it is possible that they represent deposits with very low original fossil diversities, it is assumed that the majority of impoverished samples that lie within **Cluster A** in both dendrograms (Figures 4. 1. & 4. 6.) represent the very degraded remains of fossil assemblages which were originally much more diverse. Hence, the (organically preserved) seeds

remaining in these samples are presumably more decay-resistant than those that have completely degraded and disappeared. The organically preserved seed species recovered from the **Cluster A** (Figure 4. 1.) samples comprise: *Agrostemma githago* (corncockle), *Ficus carica* (fig), *Fragaria vesca* (wild strawberry), *Rubus fruticosus* (blackberry), *Sambucus nigra* (elder), *Conium maculatum* (hemlock), *Eriophorum vaginatum* (harestail cotton grass), *Juncus bufonius* (toad rush), *Juncus gerardi* (black rush), *Sonchus asper* (prickly sow thistle), *Stachys* sp(p). (woundworts), *Atriplex* sp(p). (oraches), *Corylus avellana* (hazel), *Urtica urens* (small nettle), *Urtica dioica* (stinging nettle), *Prunus* sp(p). (plum, peach, etc.), *Carex* sp(p). (sedges), *Linum usitatissimum* (flax), *Rubus idaeus* (raspberry), *Chenopodium album* (fat hen), *Hyoscyamus niger* (henbane), *Papaver argemone* (prickly poppy), *Papaver hybridum* (? poppy), *Solanum* sp(p). (black nightshade, etc.), *Aethusa cynapium* (fool's parsley), *Conium maculatum* (hemlock), *Prunus spinosa* (blackthorn), *Atropa bella-donna* (deadly nightshade), *Centaurea* sp(p). (knapweeds), *Juncus inflexus/effusus/conglomeratus* (hard/soft/compact rush), *Raphanus raphanistrum* (wild radish), *Rumex* sp(p). (docks), *Scrophularia* sp(p). (figworts) and *Sambucus ebulus* (dwarf elder).

The preferential survival of these seeds can be attributed to structural and/or chemical features of their seed coats or endocarps. For example, the seeds of strawberries, blackberries, raspberries and plums are encased in a thick lignified endocarp (or stone), making them very robust (see **Chapter 2** for pyrolysis evidence of blackberry endocarp composition). Elder seeds are also notoriously robust, so much so that careful examination is necessary to distinguish between fossil seeds and modern contaminants in archaeological deposits (Carruthers, 2000), so although the composition of elder seed coats is not known, they are likely to have a lignified composition. Pyrolysis of *Urtica urens* (small nettle) seed coats

(see **Chapter 3**) revealed that they lack lignin and are dominated by polysaccharides, and it is likely that the closely related *Urtica dioica* (stinging nettle) seed coats are of similar composition. It may be that by exploiting a wide variety of habitats and producing numerous seeds, the nettles enhance the chances of some of their seed persisting in archaeological deposits. *Hyoscyamus niger* (henbane) seed coats are also known to have an unusual composition, comprising significant amounts of protein along with lignin (see **Chapter 3**), but the full impact of seed coat chemistry on preservation potential has yet to be established. Corncockle (*Agrostemmma githago*) seed coats have a similar composition to those of henbane (see **Chapter 2**) but their survival in apparently degraded deposits may be due partly to their presence within mineralised faecal concretions, which may protect them from significant microbial decay. Some of the species listed above occur only in one **Cluster A** sample, so that further impoverished archaeological samples need to be studied in order to distinguish those truly robust species from members of originally restricted floras. Analysis of the seed coat compositions of additional apparently robust species are also needed to establish if all decay-resistant species have lignified seed coats.

In contrast to the very scant plant assemblages present in the samples in **Cluster A**, some samples contain very diverse assemblages, in which there has presumably been little selective decay. For example, several samples contain crab apple (*Malus sylvestris*) seeds, which are known to have a non-lignified composition comprising non-hydrolysable tannins and cellulose (see **Chapter 2**). In contrast, other samples contain just crab apple endocarp (core) and seed cup bases, indicating that the seeds were originally present but have decayed. Presumably the absence of lignin from *Malus sylvestris* seed coats makes them less decay resistant than seed coats containing lignin. Further work is needed to establish which other

taxa possess non-lignified seed coats and the full impact of their composition on preservation potential. As well as studying the patterns of occurrences of different taxa in archaeological samples, decay experiments could be set up to investigate how a variety of seeds respond to a range of degradation conditions, and the impact this has for bias in archaeological samples (see **Chapter 5**, Further Work, for details).

4. 4. 1. 4. Type of deposit does not dictate the extent of decay and mineralisation

Although deposits within the same category (e. g. pit fills) might be predicted to preserve similar fossil assemblages, the results of this analysis do not support this. Some small clusters in the dendrograms do comprise samples recovered from a single deposit type (although this may be purely chance as these usually comprise pit fills, which dominate the samples overall) but many contain samples from a mixture of different deposits. For example, samples 209 through 97 in **Cluster B** comprise 2 floor deposits, 3 pit fills, a yard deposit, an indeterminate sample, and a fill from a feature within a building, yet they are united by the presence of similar fossil assemblages. This indicates that the nature of a fossil assemblage is not dictated solely by the type of deposit from which it is recovered. Where deposits preserve a very diverse (and therefore, presumably not significantly selectively decayed) fossil assemblage, it is likely that the initial input of taxa is more influential than the deposit type in determining the composition of the fossil assemblages eventually recovered by archaeologists.

Previous studies (e. g. Green, 1984) suggested that phosphatisation only occurs in association with cess pits. However, only 71% of the samples in this study which yielded mineralised remains are from pit fills; they were also recovered from a variety of other deposits, including floor deposits,

dumps/build-ups, post-hole fills, oven/fire remains and ditch/trench fills. While some of these samples may contain robust mineralised remains that have been reworked from older cess pits, a wide range of deposit types may contain mineralised remains and archaeologists should always allow for this possibility by using a processing procedure that includes examination of sieve residues, regardless of whether samples were recovered from cess pits. Mineralised remains may potentially reveal the presence of taxa that are not represented by organically preserved or charred remains, e. g. easily degraded taxa that are normally preserved only if they are replaced by calcium phosphate at an early stage.

4. 4. 1. 5. On an archaeological time-scale, the age of a deposit has no impact on preservation

Palaeontological studies have revealed that the older a deposit is, the less likely it is to yield chemically unaltered organic remains. Indeed, approximate cut-off points can be recognised in geological history, beyond which specific biomolecules do not usually survive (see **Chapter 1**). However, this analysis shows that the rule of increasing taphonomic loss in progressively older deposits does not apply on an archaeological time-scale. For example, within **Cluster A**, pit fills from as early as the Roman period (ca. AD 40-400) and as late as the 17th Century were grouped together on the basis of similarly impoverished fossil assemblages. Age variation is generally less (usually within 2 or 3 centuries) among the members of sub-clusters in **Cluster B**, although samples 152, 153 and 307 are grouped together on the basis of similar, relatively diverse fossil assemblages (Figure 4. 1.), while the ages of the deposits may be as much as 6 centuries apart. In the dendrogram based on just plant remains (Figure 4. 6.), samples 152 and 153, which are attributed to the Viking age (C9th-C11th), group with a uncertainly dated 2nd Century sample, despite being

much younger. Hence, there are huge variations in decay rate between deposits, which can result in the occurrence of similar fossil assemblages in deposits separated by over a thousand years in age. This may be explained by "decay thresholds", when groups of species with certain characteristics become totally degraded and disappear. These thresholds are reached after different periods of time in different deposits, in response to variation in the decay rate, so that deposits of vastly different ages may have reached the same decay threshold and retain similar fossil assemblages.

4. 4. 1. 6. Deposits from the same site and of the same age and type may preserve very similar or vastly different fossil assemblages

In the cluster analysis dendrograms (Figures 4. 1. & 4. 6.), some clusters are dominated by samples recovered from deposits of the same type and age on the same site. For example, samples 171, 322, 324, 325, 326 and 327 (all Viking age pit fills from St. Saviourgate in York) cluster both on the basis of their total fossil content and just their plant taxa (along with two additional samples). Another example of this is **B(iii) Part 3 (a),** comprising samples 156 to 159, a selection of indeterminate fills from (44-45) Parliament Street in York. These samples are less certain to be of the same date and type as samples 171 to 327, but nonetheless preserve very similar assemblages. These clusters suggest that site-wide parameters are more important than localised features of individual deposits in determining the nature of preservation, e. g. the height of the water table and permeability of the "parent" sediment may determine whether a deposit is consistently waterlogged or only fluctuatingly so.

More commonly, however, samples of the same age and provenance occur scattered throughout different small clusters, in some cases even in different major clusters, indicating a significant difference in their

contained fossil assemblages. An example is provided by samples 54, 55 and 34, pit fills of similar age (C14th-C15th) recovered from the Bedern in York. The first two samples fall within **Cluster A ((i) Part 1 (a))** and contain very few plant remains (9 and 3 respectively), while sample 34 lies within **Cluster B**, reflected in a very diverse plant assemblage comprising 63 taxa. This suggests that localised characteristics of individual deposits (or even different layers within the same deposit) influence preservation more than site-wide features. Possible reasons for variation within the same deposit type include differences in original input, due to distinct uses (e.g. cess versus storage pits) or deposition at different times of year (reflecting the seasonality of both edible species and background weed input), or the operation of different taphonomic processes in different deposits or at different levels within the same deposit.

4. 4. 2. Cluster analysis of common seeds and grains

The three main factors that determine the taxonomic composition of an archaeological plant assemblage are the composition of the assemblage originally deposited, the variation in the preservation potential of the taxa present, and the amount of decay that takes place in the deposit. Greig's (1981) diagram (see Figure 4. 12.) illustrating the routes taken by biological remains into a Medieval barrel latrine emphasises that the plant species recovered from an archaeological deposit may have a number of different provenances. A number of taxa are intentionally brought onto habitation sites for consumption, cloth making, bedding, medicinal purposes, and so on. In addition to those plants that have an obvious anthropological function, a large number of weed taxa are typically recovered. While some taxa, such as corncockle (*Agrostemma githago*), are clearly crop contaminants brought on-site along with the edible plants, the source of other species is not so obvious.

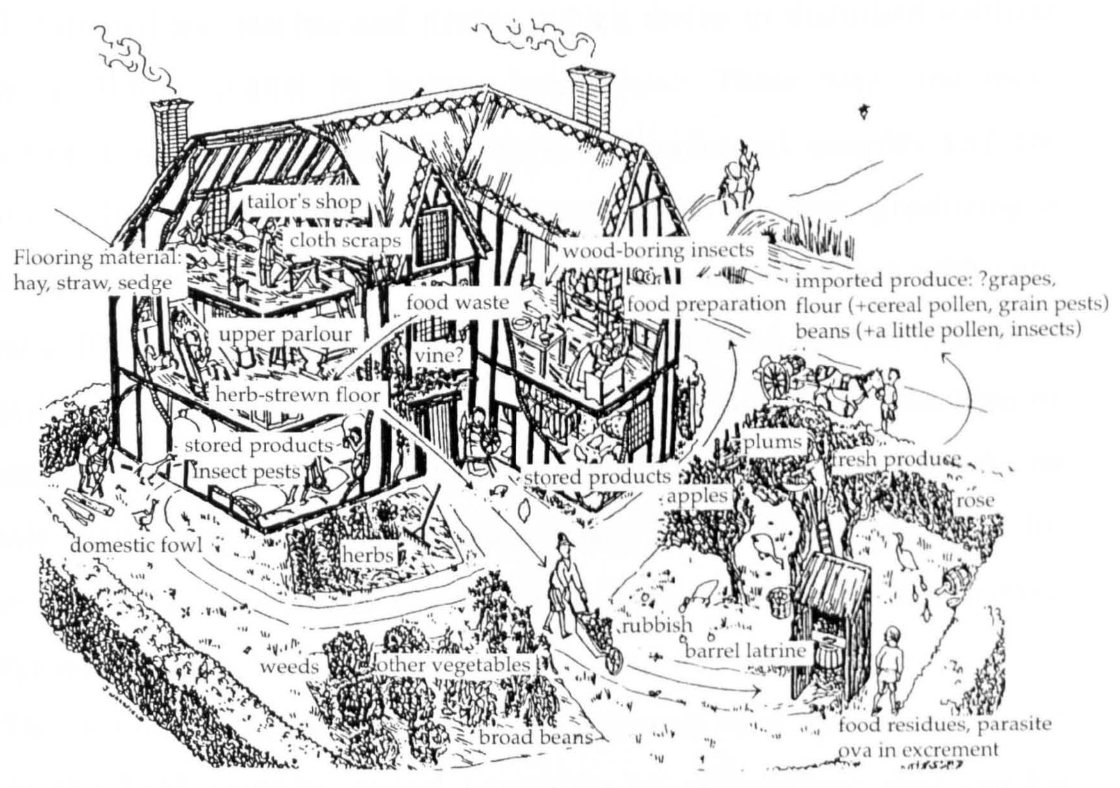


Figure 4. 12. Illustration showing the possible sources of biological remains recovered from a Medieval barrel latrine (after Greig, 1981).

Cluster A (i) (a) 1 Part One contains a number of prolific weed taxa, including sedges, oraches and nettles, which thrive in disturbed habitats such as those created by human habitation. These were the most common taxa recovered from the York archaeological samples and are likely to have grown on or around most habitation sites, producing a "background rain" of seeds. In addition to these common taxa with very general habitat preferences, there are a number of weed species with more specific requirements, which could have been introduced via a number of routes. Their seeds may have been transported from nearby habitats, or whole plants may have been carried on-site along with plants used by humans (e. g. woodland species with moss gathered for sanitary purposes).

The results of cluster analysis of the common seed species recovered from the York samples reveal a number of associations that can be explained in a variety of different ways. Some clusters contain mainly or exclusively edible plant seeds (e.g. **Cluster A (i) c**), and these were clearly brought on-site for consumption, resulting in the deposition of their seeds in cess pits or other repositories for organic waste. It is sometimes possible to attribute all the weed species within a cluster to a single modern plant community (for example, **Cluster A (i) (b) and Cluster C**) but this is rare and more typically, the assemblage must have originated from two or more distinct habitats.

In deposits which have undergone minimal organic decay, the fossil assemblage will correspond closely to the plant assemblage originally deposited, with loss of only very labile components (see Figure 4. 13.). Where more significant decay has taken place, the fossil assemblage will represent only those relatively decay resistant taxa that have survived in preference to those that are more easily degraded. In the case of seeds, the

intrinsic decay resistance of a species is likely to be dictated by structural and compositional features of its seed coat. Lignified seed coats will survive in preference to those lacking lignin. Decay thresholds may operate, such that seeds with particular coat characters disappear from fossil assemblages at different stages of decay.

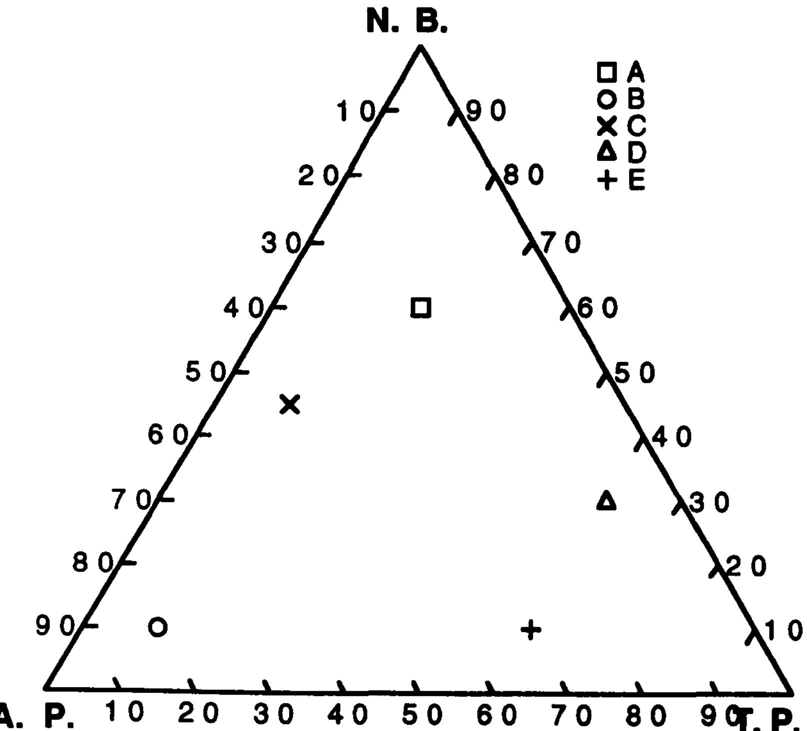


Figure 4. 13. Ternary plot illustrating the range of fossil assemblages created when varying inputs of natural background plants (weeds) versus anthropogenically introduced taxa undergo different amounts of decay.

N. B. = natural "background rain" of weeds growing wild on and around human habitation sites; A. P. = taxa introduced by anthropogenic processes, such as edible plant remains deposited in cess pits; T. P. = the taphonomic processes that selectively decay and/or mineralise the deposited plant assemblages.

Point A represents an assemblage dominated by weeds, with few anthropogenically introduced taxa, which has undergone minimal taphonomic alteration and therefore retains the bulk of the originally deposited assemblage. This assemblage might be found in a deposit which did not function in accommodating organic waste or food but which became infilled over time by weeds, such as a disused well.

Point B represents an assemblage dominated by anthropogenically introduced plant remains, with few weed taxa, which has undergone minimal taphonomic alteration. An example of this would be a well-preserved, "pure" cess pit assemblage that retains the majority of the taxa originally deposited.

Point C represents an assemblage with approximately equal contributions from weed and anthropogenically introduced taxa, which has undergone minimal taphonomic alteration, so that the majority of the original assemblage remains. Many anthropogenic deposits such as cess pits fall into this category, as they become infilled with human waste through their intended function but also receive a significant input of weed taxa growing on and around human habitation sites, and introduced as contaminants.

Point D represents an assemblage dominated by weeds, with few anthropogenically introduced taxa, which has undergone significant taphonomic alteration, resulting in selective preservation of the original assemblage. As with Point A, this assemblage is most likely to occur within a deposit which did not function in food/waste storage, such as a disused well.

Point E represents a dominantly anthropogenic assemblage, which has undergone major taphonomic alteration to selectively preserve only part of the original assemblage. A poorly preserved "pure" cess pit sample falls into this category.

Although most of the seeds included in the analysis were organically preserved, examples that frequently occur in a charred or mineralised state were included to reveal any differences in the associations in which a taxon occurred depending on its preservation state. The results of this analysis show that non-organically preserved seed species tend to occur in association with other taxa preserved in the same style. For example, charred cereals of different types occur together in **Cluster A (i) (d)**, and **Cluster F** comprises just three mineralised taxa. The association of the charred cereals is unsurprising as these would have been formed during the same crop-processing procedure, and deposited together as waste in the same rubbish or cess pit. The inertness of carbonised remains ensures that they survive for long periods after deposition, regardless of the properties of the deposit.

The association of different mineralised taxa reflects the occurrence of conditions for phosphatisation. The clustering of mineralised taxa with others that are organically-preserved (e. g. **Cluster A (i) (e)**) reflects variation in the susceptibility of different plant species to the phosphatisation process; those taxa that occur together in a mineralised state are likely to have similar "phosphatisation potentials". The likelihood of a given seed species being phosphatised under favourable conditions is probably determined by the chemical and physical features of its seed coat, and whether or not it has been subjected to cooking and/or digestion (processes that will both modify the seed coat and enhance susceptibility to decay).

5. 1. Mineralisation in archaeological deposits

5. 1. 1. The conditions required for mineralisation

Analysis of mineralised fossils and their associated sediments from ancient cess pits in and around York (Chapter 2) revealed the likely conditions favouring precipitation of calcium phosphate in archaeological deposits. Although mineralisation was not the dominant mode of preservation, and was relatively localised within these deposits, their study may still constrain the parameters under which phosphatisation takes place since they all contain at least some phosphatised remains. The relative scarcity of mineralised fossils within the samples studied is attributed to the fact that the decay rate was too low to allow widespread mineralisation, and only easily-decayed tissues were degraded rapidly enough to allow their replacement by calcium phosphate. The remaining, more recalcitrant remains underwent more gradual, slow decay, at a rate dictated by their compositional and structural characteristics (see below).

The results of elemental analysis of the phosphatised fossils and faecal concretions that were recovered from the cess pits suggest that degradation of the mineralised material took place within the Mn-reduction and Fe-reduction zones of the sediment, i.e. under anaerobic conditions near the oxic/anoxic boundary. This implies that phosphatisation may occur in any deposit with high enough P levels in which anoxia develops, even if this is only on a very localised scale. pH analysis of the sediment pore waters from the cess pits revealed that they are all mildly acidic, between pH 4 and 5, a result that is consistent with the stability range of calcium phosphate, which allows it to precipitate in acidic environments. The instability of the mineral calcium carbonate

under acidic conditions explains why fossils preserved in this mineral (the one most commonly associated with fossilisation of soft tissues) are not recovered from these deposits. The acidic conditions thought to favour calcium phosphate precipitation may develop in any deposit in which significant decay of organic matter is taking place, where the accumulation of acidic decay products results in the necessary fall in pH. It is likely that at least partial waterlogging of the soil is necessary to promote the development of anoxic and acidic conditions; in a free-draining soil, microbial processes are more likely to remain oxic.

In addition to meeting the environmental conditions in which calcium phosphate precipitation is favoured, any deposit that is to yield this mineral must also contain the necessary raw materials, calcium and phosphate ions. This does not necessarily require the presence of biomineralised material such as bones and shells. These materials may contribute ions to the phosphatisation process through dissolution; the calcium carbonate fabric of shells is unstable in the acidic conditions that favour calcium phosphate precipitation. However, although statistical analysis of the York finds data suggested a correlation between the presence of bones and mineralised remains in archaeological samples, this does not necessarily imply that the bones provided all of the ions needed for phosphatisation, nor indeed that they are involved in the mineralisation process at all. XRD analysis of the hydroxyapatite crystallinity of the bones recovered from the York cess pits (see **Chapter 2**) indicates that they have undergone only negligible alteration, indicating that they are unlikely to have contributed the ions needed for phosphatisation in these deposits. An alternative explanation for the apparent association between the preservation of bones and mineralisation is simply that the conditions that favour calcium

phosphate precipitation are also the conditions under which bones are most stable.

The most likely source of the bulk of the ions needed for phosphatisation is the abundant organic matter in the deposits. In cess pits, faecal material provides a very easily degraded food source for bacteria and decay releases the high ion concentrations needed for calcium phosphate formation. "Soft tissues" from other sources, such as the muscle, skin and entrails generated as waste from fish cleaning may also fulfil this role.

5. 1. 2. The range of deposits in which phosphatisation is likely to occur

In principle, phosphatisation may occur in any deposit that meets the criteria discussed above: (1) the conditions needed for phosphatisation must be met by rapid burial of abundant organic remains and partial waterlogging of the soil, leading to the development of areas of anoxia and acidic pore waters (created by the decay of organic matter under closed conditions) that favour precipitation of calcium phosphate; and (2) the necessary raw materials must be provided via a high rate of input of easily-degraded organic matter. Considering these criteria, it is clear why phosphatisation is most commonly associated with cess and rubbish pits, and middens; these are the main types of anthropogenic deposit into which organic-rich waste is dumped in significant quantities, along with water in the form of urine in the case of cess pits. The other main categories of archaeological deposit, such as wells and ditches, are unlikely to be organic-rich enough, at least while performing their original intended function.

Analysis of the finds database for the E. A. U. in York revealed that only 71% of those deposits yielding mineralised remains were pits. The varied array of deposits from which phosphatised material has been

recovered includes floor deposits, dumps/build-ups, post-hole fills, oven/fire remains and ditch/trench fills, although some records of mineralised remains from these may represent robust mineralised remains that have been reworked from pits. It is unsurprising that dumps or organic build-ups should occasionally yield mineralised remains; provided the material they contain is organic-rich and labile enough, they may turn anoxic and acidic in the same way as cess pits, allowing phosphatisation to take place. Such a scenario is envisaged for perhaps the most impressive mineralised archaeological deposit uncovered in Britain, the Bronze Age midden at Potterne in Wiltshire (see **Chapter 3**). Mineralisation occurs throughout the depth of the midden; as the organic remains on top became buried by the addition of more material, the newly buried level began to decay and turned anoxic/acidic, allowing phosphatisation to take place.

It is unlikely that a post hole or ditch will receive sufficient organic input to allow widespread development of the conditions required for mineralisation. However, having fallen into disuse, these deposits may be allowed to infill with organic material over time and the necessary conditions for phosphatisation may arise. These conditions need only develop on a very localised scale to affect a proportion of the organic remains present. For example, anoxia may develop over just a few millimetres of sediment.

While the conditions required for phosphatisation can be established in a variety of holes in the ground which were at some stage in their history infilled with substantial amounts of organic waste, this process may also occur in relatively thin, flat-lying deposits such as build-ups on the floors of houses or stables. That such deposits may occasionally become mineralised is illustrated by the stable floor deposit examined from 22 Piccadilly in York. It is probably significant that this sample is

thought to have become mineralised *post*-excavation, during storage, rather than while it was still in the ground, a phenomenon which suggests that these deposits may have the raw materials needed for phosphatisation but that the conditions required are not usually met. It is likely that floor build-ups are generally too thin to allow widespread development of anoxia, so that the 22 Piccadilly sample had to be sealed in a tub for several months before the oxygen in its sediment was depleted. However, where a floor build-up develops to a more substantial thickness, this may allow anoxic conditions to develop over a thin depth of sediment, potentially leading to localised phosphatisation.

Hence, although the majority of mineralised remains recovered from archaeological deposits are found in ancient cess pits, this style of preservation is encountered in a wide range of other deposit types, at least on a small scale. Phosphatised remains may preserve a range of taxa that is different to those preserved organically (through "waterlogging") or through charring, so it is important to allow for their possible presence in archaeological samples by examining sieve residues, as well as flots, where time and resources allow this.

5. 1. 3. The range of tissues most likely to be preserved by phosphatisation

It is well established that phosphatisation of soft tissues requires a delicate balance between decay of the tissues and precipitation of calcium phosphate. The decay rate within a deposit has to be just right if mineralisation is to take place: fast enough to generate the high ion concentrations needed, but not so high that everything disappears before it can be replaced with calcium phosphate. Even where the conditions required for phosphatisation are met, only certain tissues will be preserved in this way; some will degrade too quickly, others too slowly to

allow them to become mineralised. The need for a high decay rate means that it is usually those tissues that are relatively easily degraded that are preserved through phosphatisation in this study: among the plants, this is generally the embryos of seeds, among animals, the soft-bodied earthworms and maggots. Within seeds, calcium phosphate replacement was generally not fast enough to replicate the cell walls of the cotyledons before they disappeared, although phosphatised spheres which may represent nutrient bodies within the cotyledons are common. Although phosphatisation of seeds was typically restricted to the embryo, some specimens also displayed mineralisation of part or all of the seed coat. Most notably, seed coats of the small nettle (*Urtica urens*) recovered from the Bronze Age midden at Potterne were phosphatised, while the majority of the other taxa were represented only by mineralised embryos. The extent of mineralisation of the *Urtica urens* seed coat is attributed to its unusual combination of characteristics: a thin, simple structure and chemical composition apparently dominated by cellulose and hemicelluloses, which make it more easily degraded than the seed coats of the other species present. Those seed taxa represented only by mineralised embryos had a variety of seed coat compositions, and the coats were all relatively thick with complex structures, presumably making them difficult for bacteria to degrade rapidly. At a later decay stage, the coats degraded, leaving behind mineralised naked embryos. Hence, whether the coat of a particular seed is likely to become mineralised or not is determined by its relative decay resistance (which will be dictated by both structural and chemical characteristics; see 5. 2. 3. below). In addition, all of the many mineralised roots that have been examined from Potterne belong to dicotyledonous plants, despite the fact that moncotyledons are strongly represented on the site by various grasses. This is attributed to differences in the life cycle of the taxa

present; the monocots are all annuals, with roots that would have decayed rapidly after death before the conditions for mineralisation could develop, whereas some of the dicots are perennials, the more decay resistant roots of which persisted in the ground after death until the conditions favouring phosphatisation developed.

Green (1991) reported that 90 percent of mineralised plant remains recovered from archaeological deposits in southern England were food plants, a bias reflecting the fact that most deposits yielding mineralised remains are cess pits containing lots of food waste. In addition, the inclusion of a plant remain within a faecal concretion is likely to enhance its phosphatisation potential (due to being surrounded by bacteria and nutrient-rich, readily-decayed organic matter). However, the fact that most plant remains have the potential to become mineralised is revealed by the Bronze Age midden at Potterne, where the phosphatised plants are not food items but the seeds and roots of weeds which thrived on the midden and in the surrounding area.

The animals mineralised in the cess pits studied were mainly earthworms and maggots, and the majority of these were very well preserved externally but displayed only localised areas of mineralised internal soft tissue. The near-perfect replication of the external features of the outer epidermis on these animals may be attributed to the fact that this protective outer covering is more decay-resistant than the muscles and other labile tissues inside. The epidermis presumably degraded at a suitable rate to allow its replication in calcium phosphate. The internal tissues of the invertebrates generally degraded too quickly, resulting in the preservation of the body cavity as a structureless mass of crystals. However, three earthworm specimens displayed preservation of even these very labile tissues on a localised scale; both transverse and circular muscle tissue and a set of blood vessels were replaced by calcium

phosphate in these specimens, indicative of mineralisation before these delicate tissues had decayed.

Statistical analysis of the mineralised remains recorded by the E. A. U. in York indicates that the most common mineralised structures recovered are the stones of *Prunus* (plum/peach/sloe), which are very tough and recalcitrant. This suggests that the conditions needed for phosphatisation often develop at a later stage in the decay process, when the more labile structures in a deposit have totally degraded, and the most recalcitrant remains are beginning to decay at a significant rate. It may be the case that such decay-resistant structures remain relatively stable and unaltered for long periods of time, until a "decay threshold" is reached, a point at which such structures begin to degrade rapidly (perhaps in response to the presence of significant microbial populations and/or to the cleaving of key bonds in their chemical makeup). At this relatively late stage in the degradation of a deposit, pore water ion concentrations may have reached a high level which promotes precipitation of calcium phosphate, making mineralisation more likely to occur than at an early stage when labile remains still persist.

5. 1. 4. The impact of mineralisation on archaeological assemblages

The importance of mineralised fossil remains for environmental archaeological studies lies in the fact that these often represent structures or taxa that are not preserved organically or as charred remains. Those remains that are preserved through mineralisation are often relatively labile. If the conditions required for phosphatisation are not met, they simply degrade completely and disappear. Conversely, those fossil remains that persist to be recovered as organic material are relatively decay resistant and their preservation through mineral replacement is not possible.

The Bronze Age midden at Potterne in Wiltshire illustrates the potential value of mineralised remains in archaeological studies. The majority of sub-fossil remains recovered from this deposit are preserved through replacement by calcium phosphate (the remainder comprising charred remains), and no original organic material remains. Phosphatisation has preserved an impressive catalogue of seeds from 64 genera/species, representing 29 different families, and these have revealed much about the environment on and around the midden. Had conditions for mineralisation not arisen, it is likely that only a limited, carbonised portion of the flora would have survived; even given a relatively slow decay rate in the deposit, non-charred organic remains are unlikely to have persisted for the ca. 3500 years since their deposition.

5. 2. Organic preservation in archaeological deposits

5. 2. 1. Source of material versus taphonomic factors in determining the nature of archaeological sub-fossil assemblages

The composition of the fossil assemblage recovered from an archaeological deposit is determined by three main factors: (1) the assemblage originally deposited; (2) the decay rate in the deposit; and (3) the intrinsic chemical and structural characteristics of the organic remains present.

As illustrated in Greig's (1981) diagram outlining the possible sources of vegetal remains in a Medieval barrel latrine (see **Chapter 4**, Figure 4. 12.), plant remains may follow a large variety of routes into such an archaeological deposit. In addition to weeds and edible plants growing on-site, botanical products may be imported for construction material, bedding, "toilet roll" (mosses), cloth making (e. g. flax and dye plants), dietary and medicinal purposes, all bringing with them unavoidable weed contaminants. The remains of food items may find their way into

a cess pit through the obvious, human waste, route or as waste from cooking, food preparation and livestock foddering. Airborne pollen grains and seeds may be conveyed from miles around, inputting ecological signals from distant plant communities. Thus, the starting assemblage in a cess pit is likely to be a complex mixture of taxa derived from a number of different human activities and natural phenomena.

Cluster analysis of the finds data base for the E. A. U. in York (**Chapter 4**) aimed to establish the groups of plant taxa commonly found together within archaeological deposits. The results indicate that no one rule can be applied to explain the association of different groups of taxa. One cluster contained the small group of taxa that occur in most archaeological samples studied, mainly those prolific weeds which commonly invade every available scrap of disturbed and waste land in present-day Britain (e. g. nettles, docks and chickweed). However, it is not always possible to explain the co-occurrence of a cluster of taxa simply by their ecological preferences. As discussed above, a cess pit does not simply sample the plants growing in its immediate surroundings. In some cases, it is obvious that a group of plants was brought onto a site for a particular purpose, the most obvious example being clusters containing edible taxa, such as those comprising the "Medieval fruit salad" (strawberries, figs, grapes, cherries and so on) thought to be typical of cess pits from the Middle Ages. In other cases, there is no obvious functional or ecological explanation for the content of a cluster. It may be entirely coincidental, the plants just happening to find their way into the same deposits via very different routes.

A motley assemblage of plant remains may be deposited in a cess pit, via a variety of processes. The nature of the depositional environment, and intrinsic structural and compositional characteristics of the taxa present, determine which organic remains survive the centuries to be

excavated by archaeologists. There are two main preservational end-points in archaeological deposits: the entirely mineralised deposit and the entirely waterlogged deposit, which may be well-preserved or significantly decayed. Cluster analysis of the finds data base for the E. A. U., York, separated contexts (samples) into two major clusters: (1) dominantly "waterlogged", preserving diverse, mainly non-mineralised fossil assemblages, and (2) a much smaller cluster, containing samples with very few organic remains, some of which were commonly mineralised. Although this result appears to identify two main preservational categories of archaeological deposit, in reality many samples fall somewhere between these extremes, along a preservational continuum. For example, some samples in the "mineralised" cluster were very degraded but displayed no mineralisation, and some of the very diverse "waterlogged" assemblages had a few mineralised taxa alongside the organically preserved remains. A range of potential deposit types is discussed below (well- and poorly-preserved "waterlogged" deposits, completely mineralised deposits and partially mineralised deposits), although it is recognised that even these represent the end points of a preservational continuum. The broad conditions and "taphonomic stages" with which each deposit type is associated are summarised in Figure 5. 1.

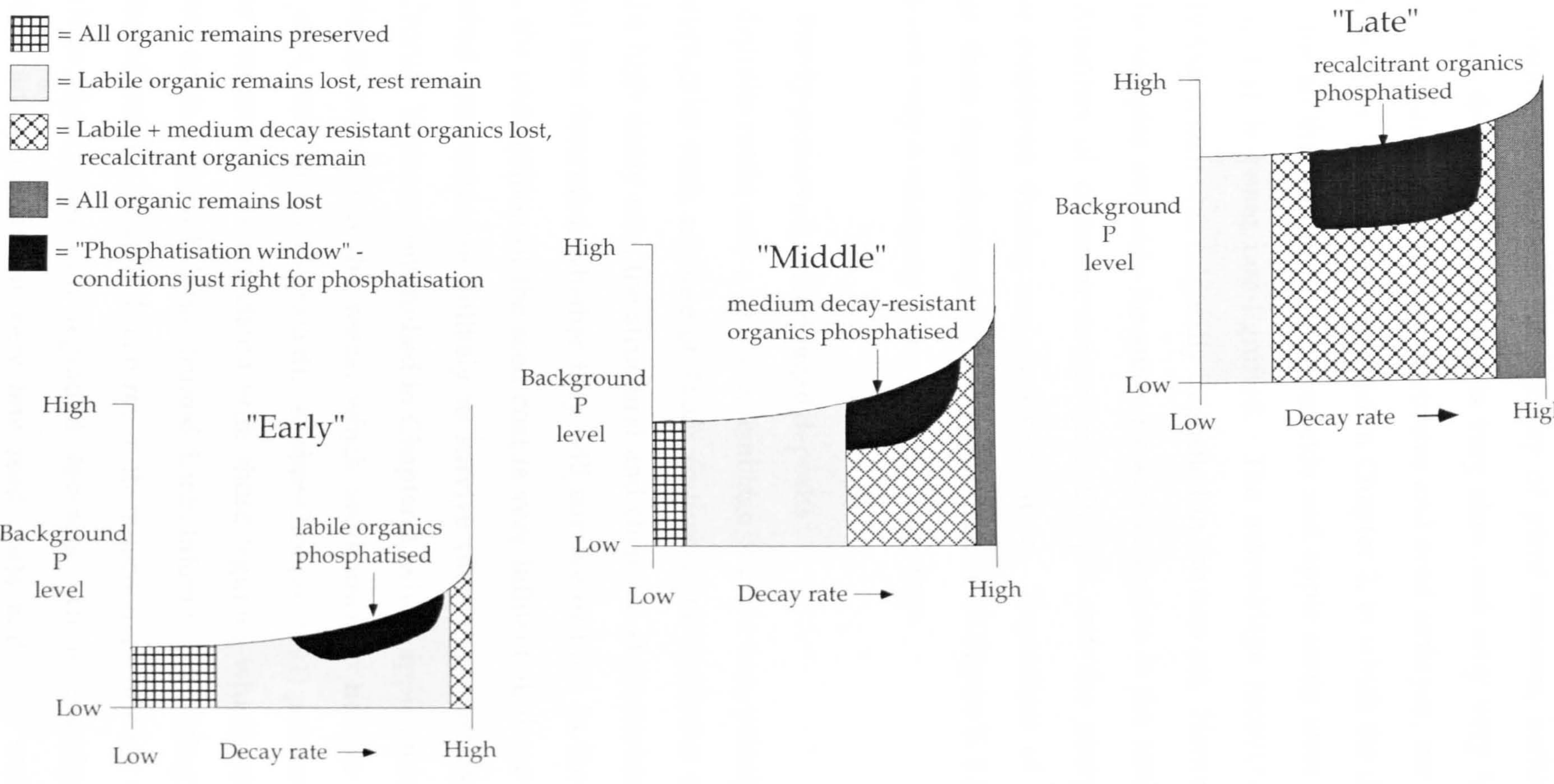


Figure 5. 1. Diagrams summarising the general preservational nature of archaeological fossil assemblages produced at "early", "middle" and "late" taphonomic stages in deposits with different decay rates and background P levels

5. 2. 1. 1. Well-preserved, waterlogged deposits

These deposits preserve a wide variety of plant remains, including those that are delicate. Decay rate is very slow and only very labile structures, such as soft-bodied invertebrates and seed embryos, are lost. An example is the York cess pits studied in **Chapter 2**, in which the decay rate was low so that the coats of corncockle and apple seeds were well preserved, despite being non-lignified. The assemblage recovered is essentially that which was originally deposited in the cess pit. Hence any bias in the samples available for study by archaeologists is the result of the combination of different routes into the pit and the sampling technique employed during and post-excavation. Regardless of their actual age, these deposits (denoted by hatched pattern in Figure 5. 1.) will have reached only a relatively "early" taphonomic stage.

5. 2. 1. 2. Poorly-preserved, waterlogged deposits

These deposits retain only a sparse assemblage of plant taxa, principally robust propagules such as those of *Rubus fruticosus* and *Sambucus nigra*. Due to the high decay rate, the structural and chemical characteristics of individual taxa determine whether they will survive or not. In the case of seeds, the composition of the seed coat is very influential; those with non-lignified seed coats are unlikely to survive (this was illustrated in the 4th Century York cess pit studied in **Chapter 2**, where apple endocarp (core) was recovered but the seeds, which are known to have a non-lignified coat, have totally degraded). Körber-Grohne (1991) pointed out that poor preservation is associated with those legumes which possess "soft" seed coats and with large fruited Umbelliferae, suggesting that compositional and/or structural features of their seed coats or fruit walls may exclude them from well-degraded deposits. Unfortunately, the composition and structure of very few seed coats and fruit walls is

known. If this information were available for all relevant taxa, it would be possible to identify groups of propagules with the same characteristics, and use this as a predictor of preservation style. Identifying such groups of propagules would allow archaeologists to recognise genuine absences from deposits where other members of the same group are present in a well-preserved state. These deposits have reached a relatively advanced taphonomic stage, denoted by a diagonally hatched pattern in Figure 5. 1.

5. 2. 1. 3. Mineralised deposits

The taphonomic history of these deposits is characterised by a high decay rate and the prevalence of conditions conducive to calcium phosphate precipitation, as outlined in **5. 1. 1.** In a deposit with widespread mineralisation, the taxa and tissues preserved are determined by their intrinsic decay resistance (which, in turn, is dictated by their compositional and structural characteristics); those which decay at an appropriate rate will be replicated by calcium phosphate as they do so, while those which decay too fast or too slowly will not be mineralised, or will be mineralised too late to retain any structural information. As indicated in Figure 5. 1., the types of organic remains that become mineralised in a deposit will depend on the "taphonomic stage" at which the conditions needed for phosphatisation develop (the "phosphatisation window" is denoted by black shading). In deposits with an initially high decay rate and background P level, very delicate organic remains may become phosphatised, but these will be lost, and more decay resistant remains mineralised, if the conditions needed do not develop until later in the deposit's history.

5. 2. 1. 4. Partially mineralised deposits

A much more common phenomenon than entirely mineralised deposits, this deposit type displays just localised phosphatisation, most commonly in the form of mineralised faecal concretions in an otherwise "waterlogged" (i.e. organically preserved) deposit. This may arise when the conditions required for phosphatisation are only met on a very localised scale, e. g. high concentrations of bacteria and readily-decayed soft tissue in faecal material may elevate the decay rate, release high ion concentrations and allow phosphatisation. In these deposits, the mineralised remains are likely to be biased towards very soft-bodied animals (maggots, etc.) and any seeds, etc. found within faecal concretions. The semi-permeable coats of some seed species may allow them to act as "ion traps", promoting phosphatisation of their embryos while little else is preserved in this way. The bias inherent in the organically preserved component of the plant assemblage will depend on the decay rate of the deposit, as discussed.

5. 2. 2. Preservation of sclerotised versus non-sclerotised insect cuticles

The insect cuticles recovered from the York cess pits (**Chapter 2**) are beetle elytra and dipteran pupal cases, and are all extremely well preserved. Pyrolysis-GC/MS revealed negligible chemical alteration: their chemical signatures were barely distinguishable from those of the modern cuticle specimens analysed for comparative purposes. However, the very high level of preservation shown by these cuticles is not representative of insect cuticle preservation in archaeological deposits, because both beetle elytra and dipteran pupal cases undergo sclerotisation during development to strengthen the cuticle. The non-sclerotised cuticles of the other insects have not survived, confirming that they have a much lower preservation potential than their sclerotised

counterparts. Although beetles and puparia reveal valuable archaeoenvironmental information, the presence of other insect groups (e. g. fleas, lice and bees) can greatly enhance our understanding of the lifestyle of our ancestors. Further work is needed on the preservation of non-sclerotised insect cuticles in archaeological deposits (see **5. 6.** below).

5. 2. 3. The impact of chemical composition on seed coat preservation

The importance of seed coat and fruit wall composition in dictating the preservation potential of propagules in fossil deposits was first recognised by van Bergen *et al.* (1994a, b & c, 1997a). The majority of angiosperm seed coats are thought to be composed of the structural polymers lignin and cellulose, and any structures which deviate from this composition generally have a lower preservation potential. Analysis of various propagules for this thesis revealed the importance of seed coat/endocarp composition in determining the nature of plant assemblages studied by environmental archaeologists. Three taxa were analysed (**Chapter 2**) and of these, only the endocarps of the blackberry (*Rubus fruticosus*) have a lignin-cellulose composition. The coats of corncockle (*Agrostemma githago*) have a protein-carbohydrate composition with little or no lignin present, while those of the crab apple (*Malus sylvestris*) are dominated by tannins and cellulose. The impact of these unusual compositions on preservational potential is clearly illustrated by the presence of apple cores (endocarp) in many archaeological samples which lack apple seeds; the non-lignified seed coats have totally degraded while many other seed coats (presumably lignified) persist. The presence of corncockle seed coats in some of the samples containing only the endocarp of apple suggests that these have a high preservation potential relative to crab apple seed coats. However, the absence of corncockle from the 4th Century cess pit (**Chapter 2**) may

indicate that these seed coats also degrade more quickly than lignified coats.

Five modern seed coat taxa were analysed to aid interpretation of the fossil assemblage from the Bronze Age midden at Potterne. The entire Potterne assemblage is mineralised and the investigation aimed to establish the basis for variation in the tissues preserved; most seeds comprised just a mineralised embryo but a minority also possessed a mineralised seed coat. Although it was predicted that just the species with the mineralised seed coat (*Urtica urens*) would have a distinct chemical composition, pyrolysis of the modern reference taxa revealed a variety of different compositions. Only one, the sedge *Carex baubuxammi*, possessed a "typical" lignin-cellulose seed coat. The seed coats of *Urtica urens* (small nettle) are unusual in being dominated by celluloses and hemicelluloses, with some proteins also present but apparently lacking lignin. Of the other three taxa analysed, the seed coats of *Brassica nigra* (black mustard) and *Hyoscyamus niger* (henbane) contain significant amounts of protein as well as lignin, and possibly also tannins, and *Chenopodium album* (fat hen) seed coats contain non-hydrolysable tannins, possibly totally lacking lignin.

Despite this variety of seed coat composition, chemistry does not appear to be the factor dictating whether or not the seed coat of a particular species became mineralised in the Potterne midden. While the lack of lignin in the *Urtica urens* seed coats undoubtedly made them less decay resistant, the thin and relatively simple structure of the coats is also thought to have been important in allowing them to decay rapidly enough to undergo phosphatisation. The thick and structurally complex coats of the other taxa would have been relatively difficult for bacteria to attack rapidly, regardless of their composition.

Seed coat composition is an important control on which taxa survive in a given deposit in original organic form: lignified coats persist for the longest periods. However, in mineralised deposits, the structure of the coat may also be a contributing factor that determines which seed taxa decay rapidly enough to become replicated in calcium phosphate.

5. 3. Preservation of bones in archaeological deposits

Bones from two major depositional settings were analysed (**Chapter 2**); those fish and small mammal bones that are common components of cess and rubbish pit infills, and human skeletal remains from a Medieval graveyard. Analysis of the bones from these very distinct settings aimed to establish the relative quality of their preservation, by characterising the changes in crystallinity of their mineral (hydroxyapatite) component. The results of the analyses revealed negligible hydroxyapatite alteration in the cess pit bones, which were virtually indistinguishable from modern bone. The graveyard bones, on the other hand, were more significantly altered; more marked alteration occurred in those skeletons that had not been coffined, compared with coffined burials. The differences in the extent of hydroxyapatite alteration in cess pit versus graveyard and coffined versus non-coffined bones are attributed to differences in the hydrological regime. In waterlogged cess pits, alteration of bone hydroxyapatite occurs mainly through diffusion of ions along concentration gradients. However, where pore water concentrations of calcium and phosphate were high enough to allow at least localised precipitation of calcium phosphate, there would be no concentration gradient along which ions could leave the bones. In graveyard sediments, which are more freely draining, alteration of the bone hydroxyapatite would occur mainly through the periodic downward flux of soil pore waters. This process is more prevalent in

non-coffined burials, whereas skeletons within coffins could become waterlogged, reducing diffusion and consequent hydroxyapatite alteration.

5. 4. Implications for environmental archaeology

The preservational processes in operation in archaeological deposits have a profound impact on the sub-fossil assemblages available for environmental archaeological study. Only in very well preserved "waterlogged" deposits will the recovered assemblage be a true reflection of that originally present. If an organically-preserved assemblage has undergone significant decay, then some of the taxa which were originally deposited will have disappeared as a result of their relatively low preservation potential. In the case of seed coats, those with a non-lignified composition will be lost once a particular "decay threshold" is reached, while those containing lignin will persist much longer. Among non-lignified coats, different compositions will be reflected in different decay resistance, so that seeds with particular coat types will "drop out" of the assemblage at different stages in degradation of the deposit.

In deposits where the conditions required for phosphatisation are met, some taxa which would otherwise be lost to decay may be preserved. The taxa that become mineralised will depend on the stage of decay reached when conditions develop that favour mineral precipitation. If this occurs at an early stage of decay, relatively labile structures that would normally disappear may become mineralised. However, if the onset of mineralisation occurs at a late stage in the degradation of a deposit, labile organic remains will already have been lost and only relatively recalcitrant structures will be preserved.

Cluster analysis of part of the finds database for the E. A. U. in York revealed that there are no clear rules dictating the nature of assemblages

preserved in deposits of different types and/or ages. Two deposits of the same type and age (and even from the same site) may yield distinct fossil assemblages that have been moulded by very different preservational histories. Hence, different preservational processes may mean the difference between a well-preserved fossil assemblage that reveals much about the original deposit and its surrounding environment, and one in which few, recalcitrant remains persist to give a very biased view.

This study has revealed the conditions under which mineralisation is likely to occur in archaeological deposits, and the range of deposits and tissues likely to be affected. In addition, the influence of seed coat composition and structure on the preservation of fossil plant assemblages was clearly illustrated by the different organically-preserved taxa preserved in the York ancient cess pits (**Chapter 2**) and those mineralised at Potterne (**Chapter 3**). Further work in this area would reveal "preservational groups" of propagule with different seed coat/endocarp structures and compositions, which are likely to be preserved in a similar way to those studied. Hence, it may be possible in the future to distinguish between genuine absences from fossil assemblages and disappearance of taxa due to preferential decay/mineralisation.

5. 5. Implications for study of the ancient fossil record

Although this study has focused on the preservation of *sub*-fossil remains in archaeological deposits, the results have the potential to increase our understanding of fossilisation in more ancient deposits, of geological age. The early diagenetic processes manifest in archaeological sub-fossil material are the same as those that shaped the earliest, and arguably most vital, stages in fossilisation of much older deposits.

Study of phosphatised remains from archaeological deposits has revealed that mineralisation occurs under conditions in terrestrial deposits similar to those in marine settings. Although phosphatised remains have yet to be recovered from terrestrial sediments of geological age, the potential for such discoveries exists. The lack of known phosphatised plant remains of geological age is attributed to the need for an external source of ions to promote phosphatisation; the plant material does not contain enough phosphate. Fossil plant remains are usually deposited in ancient sediments where animals are absent, and there is generally not enough phosphorus present to allow mineralisation. This process would be predicted to occur in a geological deposit in which abundant soft bodied animals (or vertebrate carcasses with soft tissues still present) were deposited along with the plant material.

The impact of the composition of seed coats and endocarps on their preservation in fossil sediments has been revealed by the work of van Bergen *et al.* (1994 a, b & c, 1997a) This study increases our knowledge of this area by revealing the compositions of various seed coats and their impact on preservation potential. For example, the coats of crab apple seeds have a tannin-cellulose composition (**Chapter 2**), which accounts for their disappearance from archaeological deposits where crab apple endocarp and other seed coats persist. This selective decay also explains why no apple seeds have been found in geological deposits, despite the fact that fossil remains of the family (Roseaceae) to which they belong are known as far back as the Late Cretaceous. In contrast, blackberry endocarps have a more typical lignin-cellulose composition (**Chapter 2**) and these are found as fossils from the Eocene to the present-day (Collinson, *pers comm.*, 2000). Clearly, explanations for biases in the ancient fossil record can be accessed via the study of the early stages of degradation in deposits of archaeological age.

5. 6. Suggestions for future work

5. 6. 1. Experimental study of mineralisation in archaeological deposits

Study of the mineralised sub-fossils and faecal concretions from the York cess pits, and their surrounding sediments, revealed the likely conditions under which phosphatisation takes place in such archaeological deposits. However, the full range of conditions over which this process occurs, and indeed how quickly it happens, can only be established accurately through laboratory experiments that simulate cess pit conditions.

Experiments (Briggs & Kear, 1994a) have successfully reconstructed the conditions under which shrimp muscle tissue and other soft tissues become phosphatised under marine conditions and these have greatly increased our understanding of the controls on the preservation of such fossils in ancient marine sediments. Further work is required to establish how and why these conditions arise in terrestrial archaeological settings. The shrimp experiments provide some indication of the length of time over which arthropods must be phosphatised, the timescale over which seeds become replaced by minerals is unknown. Gill Campbell of English Heritage is in the process of setting up experiments to investigate seed phosphatisation, incorporating the results of this study. The experiments will monitor the fate of a known, dead seed assemblage over several months in various sediments (with and without various combinations of manure, fish cleaning waste and shells). While the experimental design is simple, it is a very useful first step and, assuming that phosphatisation is initiated in at least one of the sediments, will indicate the conditions required and the approximate timescale involved. More tightly constrained experiments, in which the various properties of the sediment are more closely controlled and monitored, could then be set up to yield more precise information.

Such experiments could reveal the full range of potential conditions (and by implication, broad deposit types) under which remains are phosphatised. This would alert environmental archaeologists to the need for including examination of sieve residues in their sediment processing procedure. In addition, the presence of mineralised remains in a deposit could be used to interpret the likely burial conditions.

5. 6. 2. Experimental study of the impact of digestion on seed preservation in cess pits

The majority of the seeds studied in this thesis were recovered from cess pits and a significant proportion of them are likely to have passed through a human gut. Phosphatised seeds occur within mineralised faecal concretions in deposits which lack other mineralised remains. In addition, cess pits in which no mineralisation has taken place often contain some digested seeds from both edible plants and food contaminants, such as corncockle. Various plant species achieve dispersal by packaging their seeds within juicy fruits which are attractive food items for birds and mammals (including humans). In these species, digestion may serve the important function of damaging the seed coat, facilitating germination once the seeds reach soil. It is likely that any damage to the seed coat will accelerate its degradation and may facilitate embryo mineralisation by increasing permeability. So far there have been no studies aimed at establishing the impact of digestion on seed preservation in cess pits.

A useful experiment would involve ingesting the seeds of a range of edible plants and their contaminants. The recovered seeds could then be examined for any damage, before being experimentally decayed along with non-digested control seeds to assess the impact of digestion on decay rate. While human subjects would be preferable, dogs would also be

useful, since they commonly share human occupation sites and food, and it is not unusual to recover their faecal remains from cess pits. A selection could be made to reveal the impact of digestion on the full range of seed coat compositions.

The impact of different food processing and cooking procedures on seed preservation could be investigated in a similar way, although the majority of edible fruits are likely to have been eaten with no preparation.

5. 6. 3. Study of the decay of non-lignified seed coats

While it was thought that the majority of seed coats are composed of lignin and cellulose (van Bergen *et al.*, 1994a) the wide variety of compositions revealed in this study suggests that many seed coats deviate from the "norm", and this is likely to have a significant impact on their preservation potential.

Seed coats that lack the resistant biopolymer lignin are unlikely to survive as long as lignified seed coats, a fact illustrated by the crab apple remains recovered from the York cess pits. Py-GC/MS of crab apple seed coats reveals the presence of tannins but a (perhaps even total) lack of lignins. Some deposits preserve just the endocarp that makes up the apple core, while the seeds inside have completely degraded. Hence, this particular type of non-lignified seed coat may decay completely on an archaeological timescale, and the details of the degradation process are accessible through study of archaeological sub-fossil seeds. Selective phosphatisation of the non-lignified seed coats of *Urtica urens* at Potterne illustrates the impact of chemical composition on which tissues are preserved through mineralisation. Pyrolysis of the seed coats of *Agrostemma githago* (corncockle), *Brassica nigra* (black mustard) and *Hyoscyamus niger* (henbane) revealed a significant protein component,

presumably resulting in a different response to decay than that of lignified and tannin-containing seed coats.

In addition to studying archaeological sub-fossil seeds representing various stages of degradation, experiments could be set up to replicate decay of the archaeological seeds. Seed taxa representing each known seed coat composition (ligno-cellulose, tannins-cellulose, proteins-polysaccharide, etc.) would be buried in a variety of sediment types. Samples of each species would then be removed from the sediments at regular intervals, and chemical and structural analyses carried out to establish the extent and nature of degradation. Such experiments would lead to a fuller understanding of the impact of seed coat composition on preservational bias in archaeological plant assemblages. The information obtained could also be applied directly to interpreting such biases in the ancient fossil record.

5. 6. 4. Study of non-sclerotised arthropod cuticle remains in archaeological deposits

The sub-fossil insect remains studied in this thesis all comprise sclerotised cuticles of beetles and dipteran fly puparia. The other major groups of insects (e.g. fleas, bees, crickets, lice) are not represented, presumably because their non-sclerotised cuticle has totally degraded. However, rare archaeological deposits preserve the cuticle remains of these groups. Future work on the preservation of arthropod cuticles in archaeological deposits should target those deposits yielding "rare" cuticles, in order to better understand the depositional characteristics that favour preservation of the range of insect cuticle compositions.

Although insect remains were included in the York finds database which was subjected to cluster analysis (**Chapter 4**), they were listed as very broad taxonomic groups, such as "beetle". Where time and

resources allowed, these insects would have been identified more precisely. Compilation and analysis of a database containing completely identified insect remains from archaeological deposits would allow a fuller understanding of the relative preservation potential of different insects.

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APPENDIX ONE: Full list of the fossil remains idenitified at the Environmental Archaeology Unit, University of York in the cess pit samples studied in Chapter 2.

76-81.7/18529/1019:

Fossil taxa:	Relative abundance:
Plants:	
Triticum/Secale ('bran' fragments)	3
Prunus domestica	3
Prunus spinosa	3
Crataegus monogyna	2
Isothecium myurum	2
Malus sylvestris (mineralised)	2
Neckera complanata	2
Rubus fruticosus	2
Aethusa cynapium	1
Agrostemma githago	1
Agrostemma githago (seed fragments)	1
Anethum graveolens	1
Anomodon viticulosus	1
Anthemis cotula	1
Antitrichia curtipendula	1
Atriplex sp(p).	1
Brassica rapa	1
Brassica sp(p).	1
Calluna vulgaris (capsules)	1
Calluna vulgaris (twig fragments)	1
Caltha palustris	1
Carex sp(p).	1
Chenopodium album	1
Corylus avellana	1
Diphasium complanatum	1
Eleocharis palustris	1
Eurhynchium praelongum	1
Eurhynchium striatum	1
Galium aparine	1
Genista tinctoria (stem fragments)	1
Gramineae (culm nodes)	1
Homalia trichomanoides	1
Homalothecium sp(p).	1
Humulus lupulus	1
Hylocomium splendens	1
Hypnum cupressiforme	1
Ilex aquifolium (leaf)	1
Isothecium myosuroides	1
Juglans regia	1
Juncus bufonius	1
Lapsana communis	1
Leucodon sciuroides	1
Linum usitatissimum	1
Malus sylvestris (endocarp)	1
Neckera crispa	1
Papaver somniferum	1
Picris hieracioides	1
Polygonum aviculare	1

Polygonum hydropiper	1
Polygonum lapathifolium	1
Polygonum persicaria	1
Populus sp(p). (buds.bud scales)	1
Potentilla sp(p).	1
Quercus sp(p). (buds/bud scales)	1
Ranunculus Section Ranunculus	1

76-81.7/18529/1019

Fossil taxa

Plants:

Raphanus raphanistrum (pod segments/fragments)	1
Rosa sp(p)	1
Rubia tinctorum	1
Rubus caesius	1
Rubus idaeus	1
Sambucus nigra	1
Satureja hortensis	1
Secale cereale	1
Silene alba	1
Solanum nigrum	1
Sonchus asper	1
Sonchus oleraceus	1
Sorbus aucuparia	1
Spergula arvensis	1
Stellaria media	1
Thuidium tamariscinum	1
Triticum aestivo-compactum	1
Triticum/Secale (waterlogged)	1
Ulota sp(p).	1
Urtica urens	1
Vaccinium sp(p).	1
cf. *Avena sativa*	1
cf. *Pastinaca sativa*	1
cf. *Prunus padus*	1
cf. *Vicia faba* (charred cotyledons)	1
dicot leaf fragments	1
Vertebrate remains:	
feather fragments	1
wool fragments	1
Invertebrate remains:	
earthworm egg capsules	1
eggshell membrane fragments	1
Miscellaneous:	
faecal concretions	2

BJT98/213/11

Fossil taxa

Plants:	
Triticum/Secale ('bran' fragments)	4
Agrostemma githago	2
Atriplex sp(p).	1
Brassica rapa	1
Capsella bursa-pastoris	1
Carex sp(p).	1
Centaurea cf. scabiosa	1
Cyperaceae (papillose epidermis)	1
Euphrasia sp./Odontites verna	1
Gramineae	1
Juncus sp(p).	1
Malus sylvestris (endocarp)	1
Mentha sp(p).	1
Montia fontana ssp. chondrosperma	1
Papaver argemone	1
Papaver somniferum	1
Polygonum lapathifolium	1
Prunus domestica sssp. insititia	1
Prunus Section Cerasus	1
Prunus spinosa	1
Reseda luteola	1
Rorippa palustris	1
Scandix pecten-veneris	1
Stellaria media	1
Torilis japonica	1
Urtica dioica	1
Urtica urens	1
Vertebrate remains:	
bone fgts	1
Invertebrate remains:	
earthworm egg capsules	1
Trichuris (eggs)	1
beetles	
Miscellaneous:	
charred herbaceous detritus	1
faecal concretions	1
sand	1

95.434/2037/64

Fossil taxa:

Plants:	
Triticum/Secale ('bran' fragments)	4
Agrostemma githago	3
Agrostemma githago (seed fragments)	2
Allium porrum (leaf)	2
Centaurea cf. scabiosa	2
Atriplex sp(p).	1
Bupleurum rotundifolium	1
Centaurea cyanus	1
Galium aparine	1
Malus sylvestris (endocarp)	1
Poaceae (mineralised grain)	1
Prunella vulgaris	1
Rubus idaeus	1
Rumex acetosella	1
Urtica dioica	1
Vertebrate remains:	
fish bone	1
Invertebrate remains:	
none recovered	
Miscellaneous:	
faecal concretions	3
amorphous organic matter	2
charcoal	1
herbaceous detritus	1
sand	1

95.434/1064/17

Fossil taxa:

Plants:

Triticum/Secale ('bran' fragments)	4
Agrostemma githago (seed fragments)	3
Ficus carica	2
Malus sylvestris	2
Malus sylvestris (endocarp)	2
Brassica sp(p).	1
Centaurea cyanus	1
Centaurea sp(p). (achene fragments)	1
Erica sp(p). (leaves)	1
Fragaria vesca	1
Hypnum cf. cupressiforme	1
Juncus sp(p).	1
Lapsana communis	1
Leontodon sp(p).	1
Linum usitatissimum	1
Linum usitatissimum (capsule fragments)	1
Linum usitatissimum (leaf/stem epidermis fragments)	1
Ranunculus Section Ranunculus	1
Reseda luteola	1
Rosa sp(p). (prickles)	1
Rumex acetosella	1
Rumex sp(p).	1
Silene vulgaris	1
Sphagnum Section Acutifolia	1
Sphagnam Section Sphagnum	1

Vertebrate remains:

bone fragments	1
fish scale	1
eggshell membrane fragments	1
fish bone	1

Invertebrate remains:

centipede	1
beetles	1

Miscellaneous:

faecal concretions	2
bark fragments	1
brick/tile	1
charcoal	1
dicot stem fragments	1
leather fragments	1
twig fragments	1
wood chips	1
wood fragments	1

95.434/3105/105

Fossil taxa:

Plants:

Atriplex sp(p).	2
Prunus spinosa	2
Triticum/Secale ('bran' fragments)	2
Urtica dioica	2
Anagallis arvensis	1
Brassica sp(p).	1
Carduus/Cirsium sp(p).	1
Cerastium sp(p).	1
Chenopodium sp(p).	1
Conium maculatum	1
Malus sylvestris (endocarp)	1
Malus sylvestris (seed base cups)	1
Polygonum aviculare	1
Potentilla cf. erecta	1
Rubus fruticosus agg.	1
Rubus idaeus	1
Sambucus nigra	1
Sphagnum Section Acutifolia	1
Umbelliferae	1
Urtica urens	1

Vertebrate remains:

bone fragments	1
burnt bone fragments	1
fish bone	1

Invertebrate remains:

insects	2
beetles	1
fly puparia	1

Miscellaneous:

amorphous organic matter	2
faecal concretions	2
wood fragments	2
brick/tile	1
charcoal	1
eggshell membrane fragments	1
glassy slag	1
gravel	1
herbaceous detritus	1
herbaceous detritus (charred)	1
mortar	1
sand	1

95.434/1059/15

Fossil taxa:

Plants:

Triticum/Secale ('bran' fragments)	4
Agrostemma githago (seed fragments)	3
Centaurea cyanus	2
Ficus carica	2
Reseda luteola	2
Atriplex sp(p).	1
Brassica sp(p).	1
Chrysanthemum segetum	1
Corylus avellana	1
Erica tetralix (mineralised leaves)	1
Fragaria vesca	1
Galeopsis Subgenus Galeopsis	1
Gramineae	1
Juncus sp(p).	1
Malus sylvestris (endocarp)	1
Ranunculus flammula	1
Rumex sp(p).	1
Sonchus oleraceus	1
Thlaspi arvense	1
Triticum (mineralised grain)	1
Urtica dioica	1
Vaccinium sp(p).	1

Vertebrate remains:

bone fragments	2
bird bone	1
fish scale	1
fish bone	1

Invertebrate remains:

fly puparia	2
earthworm egg capsules	1
snails	1
beetles	1

Miscellaneous:

faecal concretions	3
sand	2
'char'	1
brick/tile	1
charcoal	1
gravel	1
mortar	1
twig fragments (mineralised)	1
wood fragments	1

APPENDIX TWO: Composition of Widdels freshwater used as a medium in the laboratory decay of *Manduca sexta.*

Widdels artificial freshwater (Widdel and Bak, 1992) was used as the medium for both producing the inoculum for the laboratory decay of *Manduca sexta* and carrying out the decay itself. The medium had the following composition:

Compound:	**Concentration (g/l):**
potassium dihydrogen phosphate	0.2
ammonium chloride	0.25
sodium chloride	1.0
magnesium chloride	0.4
potassium chloride	0.5
calcium chloride	0.1

Sterile additions:	
vitamin solution	3 ml
selenite/tungstate solution	2 ml
trace element solution	2 ml
sodium bicarbonate solution	30ml

APPENDIX THREE: Grain size distributions of the cess pit sediment samples, generated by the MASTERSIZER

MALVERN INSTRUMENTS MASTERSIZER

Result Derived Diameters Report

Sample Details

Sample ID: BJT98;213;5.11 | Run Number: 2 | Measured: Wed, Nov 04, 1998 10:53AM
Sample File: (Result Not Saved) | Analysed: Wed, Nov 04, 1998 10:53AM
Sample Path: A:\ | Result Source: Analysed
Sample Notes:

System Details

Range Lens: 100 mm | Beam Length: 2.40 mm | Sampler: None | Obscuration: 45.6 %
Presentation: 4OHD | [Particle R.I. = (1.5295, 0.1000); Dispersant R.I. = 1.3300]
Analysis Model: Polydisperse | Residual: 0.393 %
Modifications: None

Result Statistics

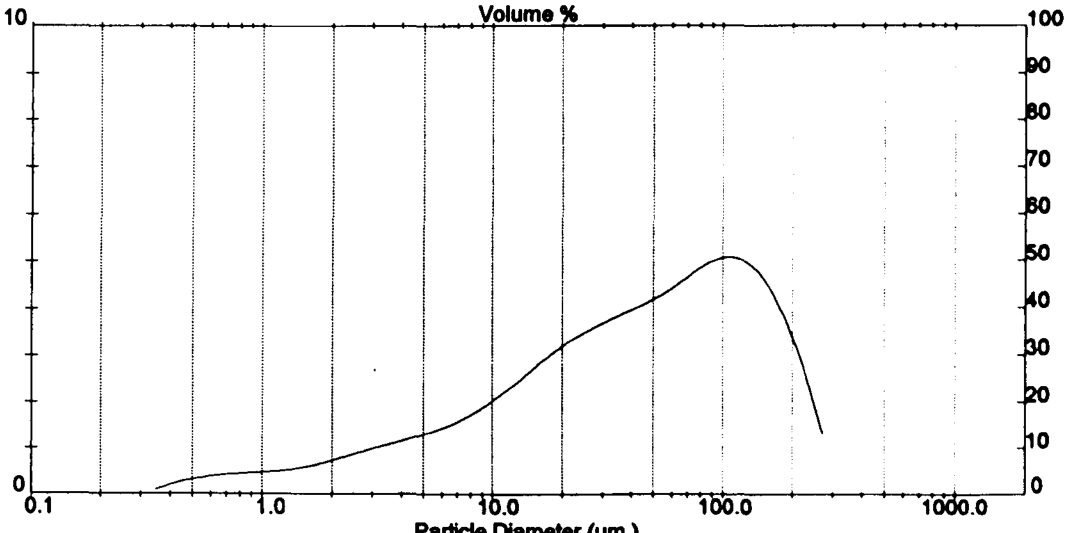
Distribution Type: Volume | Concentration = 0.0860 %Vol | Density = 1.000 g / cub. cm | Specific S.A. = 0.6549 sq. m / g
Span = 3.594E+00 | Uniformity = 1.108E+00

A.S.T.M Derived Diameters (um)				
N	3	2	1	0
D[4, N]	67.85	24.93	8.88	4.53
D[3, N]		9.16	3.21	1.64
D[2, N]			1.13	0.82
D[1, N]				0.60

Distribution Moments				
	Mean	Stan. Dev.	Skewness	Kurtosis
Volume	67.85	65.658	1.1642	0.6631
Surface	9.16	23.188	5.3038	35.8069
Length	1.13	3.008	24.5427	1082.7957
Number	0.60	0.562	30.5762	4088.1677

Distribution Percentiles (um) – Volume			
Percentile	Size	Percentile	Size
10.0 %	4.31	80.0 %	121.12
20.0 %	11.14	90.0 %	167.57
50.0 %	45.43		

Distribution Modal Sizes (um)			
Mode	Size	Mode	Size
1	106.92		



Result Derived Diameters Report

Sample Details

Sample ID: BJT98;213;5.11
Sample File: (Result Not Saved)
Sample Path: A:\
Sample Notes:

Run Number: 2

Measured: Wed, Nov 04, 1998 10:53AM
Analysed: Wed, Nov 04, 1998 10:53AM
Result Source: Analysed

System Details

Range Lens: 100 mm
Presentation: 4OHD
Analysis Model: Polydisperse
Modifications: None

Beam Length: 2.40 mm
[Particle R.I. = (1.5295, 0.1000); Dispersant R.I. = 1.3300]

Sampler: None

Obscuration: 45.6 %
Residual: 0.393 %

Result Statistics

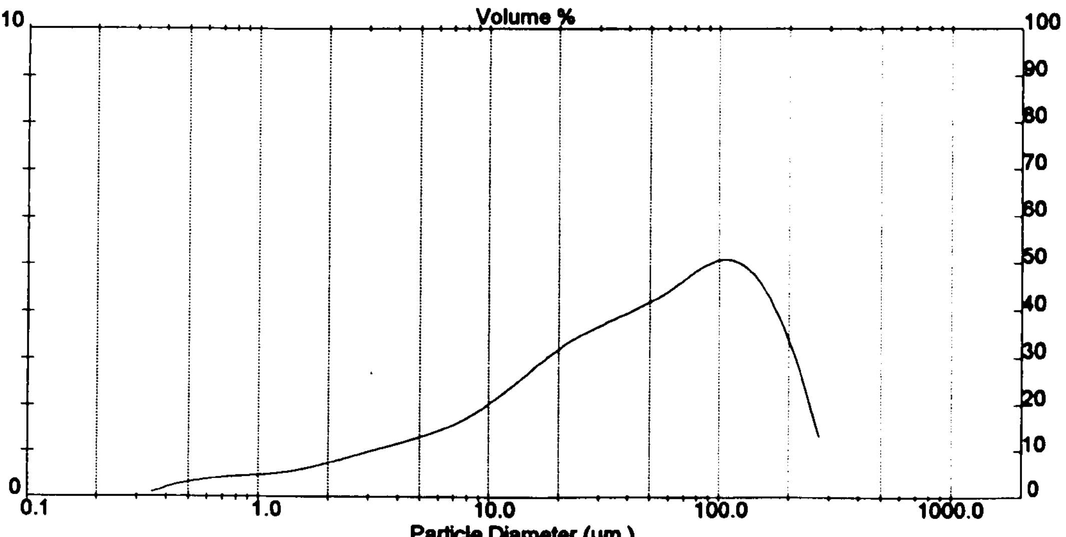
Distribution Type: Volume
Concentration = 0.0860 %Vol
Span = 3.594E+00
Density = 1.000 g / cub. cm
Uniformity = 1.108E+00
Specific S.A. = 0.6549 sq. m / g

A.S.T.M Derived Diameters (um)				
N	3	2	1	0
D[4, N]	67.85	24.93	8.88	4.53
D[3, N]		9.16	3.21	1.84
D[2, N]			1.13	0.82
D[1, N]				0.60

Distribution Moments				
	Mean	Stan. Dev.	Skewness	Kurtosis
Volume	67.85	65.658	1.1642	0.6631
Surface	9.16	23.188	5.3038	35.8069
Length	1.13	3.008	24.5427	1082.7957
Number	0.60	0.562	30.5762	4088.1677

Distribution Percentiles (um) -- Volume			
Percentile	Size	Percentile	Size
10.0 %	4.31	80.0 %	121.12
20.0 %	11.14	90.0 %	167.57
50.0 %	45.43		

Distribution Modal Sizes (um)			
Mode	Size	Mode	Size
1	106.92		



Result Derived Diameters Report

Sample Details

Sample ID: BJT98;213;5.11 | Run Number: 3 | Measured: Wed, Nov 04, 1998 10:56AM
Sample File: (Result Not Saved) | Analysed: Wed, Nov 04, 1998 10:56AM
Sample Path: A:\ | Result Source: Analysed
Sample Notes:

System Details

Range Lens: 100 mm | Beam Length: 2.40 mm | Sampler: None | Obscuration: 48.0 %
Presentation: 4OHD | [Particle R.I. = (1.5295, 0.1000); Dispersant R.I. = 1.3300]
Analysis Model: Polydisperse | Residual: 0.371 %
Modifications: None

Result Statistics

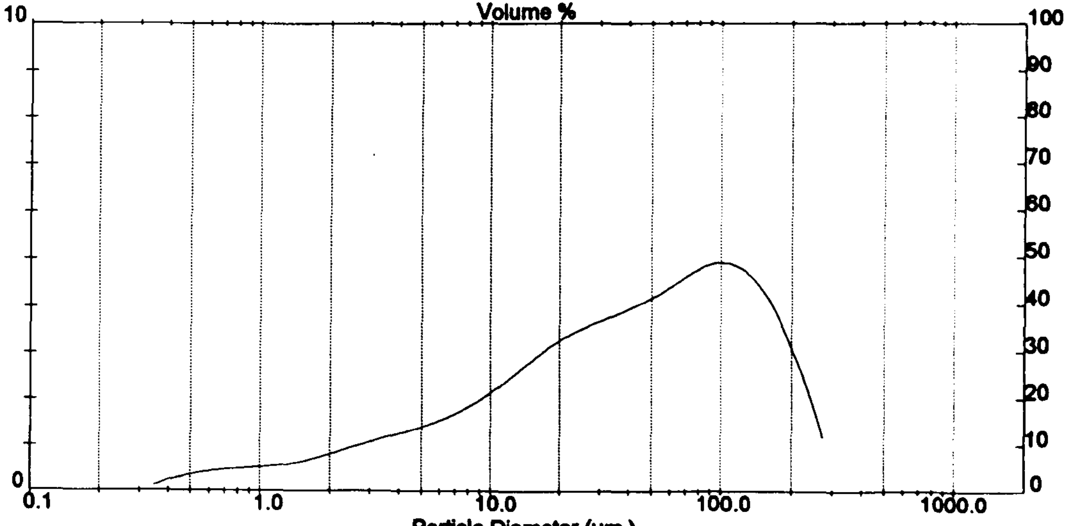
Distribution Type: Volume | Concentration = 0.0856 %Vol | Density = 1.000 g / cub. cm | Specific S.A. = 0.7082 sq. m / g
Span = 3.767E+00 | Uniformity = 1.161E+00

A.S.T.M Derived Diameters (um)				
N	3	2	1	0
D[4, N]	64.73	23.42	8.46	4.37
D[3, N]		8.47	3.06	1.78
D[2, N]			1.10	0.81
D[1, N]				0.60

Distribution Moments				
	Mean	Stan. Dev.	Skewness	Kurtosis
Volume	64.73	64.367	1.2310	0.8751
Surface	8.47	21.831	5.5623	39.8045
Length	1.10	2.852	24.8759	1135.4854
Number	0.60	0.550	29.1799	3834.3682

Distribution Percentiles (um) – Volume			
Percentile	Size	Percentile	Size
10.0 %	3.83	80.0 %	115.68
20.0 %	9.92	90.0 %	162.19
50.0 %	42.03		

Distribution Modal Sizes (um)			
Mode	Size	Mode	Size
1	100.91		



Malvern Instruments Inc.
Southborough MA, USA
Tel:508 480 0200 Fax:508 460 9692

Mastersizer µ Ver. 2.12
Serial Number: 33031-20

MALVERN INSTRUMENTS MASTERSIZER

Sample Details

Sample ID: 95.4.34;1064;5.17
Sample File: (Result Not Saved)
Sample Path: A:\
Sample Notes:

Run Number: 1

Measured: Wed, Nov 04, 1998 11:07AM
Analysed: Wed, Nov 04, 1998 11:07AM
Result Source: Analysed

System Details

Range Lens: 100 mm
Presentation: 4OHD
Analysis Model: Polydisperse
Modifications: None

Beam Length: 2.40 mm
[Particle R.I. = (1.5295, 0.1000); Dispersant R.I. = 1.3300]

Sampler: None

Obscuration: 40.2 %
Residual: 0.442 %

Result Statistics

Distribution Type: Volume
Concentration = 0.0987 %Vol
Span = 2.384E+00
Density = 1.000 g / cub. cm
Uniformity = 7.597E-01
Specific S.A. = 0.4764 sq. m / g

A.S.T.M Derived Diameters (um)

N	3	2	1	0
D[4, N]	95.53	34.68	11.20	5.42
D[3, N]		12.59	3.83	2.08
D[2, N]			1.17	0.85
D[1, N]				0.62

Distribution Moments

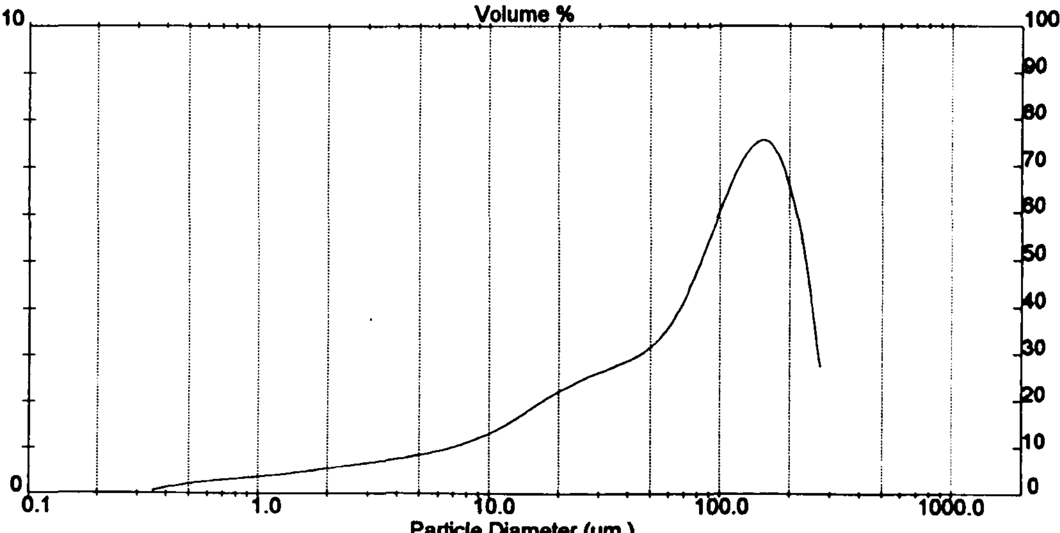
	Mean	Stan. Dev.	Skewness	Kurtosis
Volume	95.53	75.766	0.5755	-0.6641
Surface	12.59	32.318	4.3183	21.2809
Length	1.17	3.651	27.8432	1189.7450
Number	0.62	0.582	41.4925	7334.6001

Distribution Percentiles (um) -- Volume

Percentile	Size	Percentile	Size
10.0 %	6.94	80.0 %	166.38
20.0 %	19.00	90.0 %	206.65
50.0 %	83.76		

Distribution Modal Sizes (um)

Mode	Size	Mode	Size
1	154.90		



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Southborough MA, USA
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Mastersizer µ Ver. 2.12
Serial Number: 33031-20

MALVERN INSTRUMENTS MASTERSIZER

Result Derived Diameters Report

Sample Details

Sample ID: 95.4.34;1064;5.17 — Run Number: 2 — Measured: Wed, Nov 04, 1998 11:11AM
Sample File: (Result Not Saved) — Analysed: Wed, Nov 04, 1998 11:11AM
Sample Path: A:\ — Result Source: Analysed
Sample Notes:

System Details

Range Lens: 100 mm — Beam Length: 2.40 mm — Sampler: None — Obscuration: 42.8 %
Presentation: 4OHD — [Particle R.I. = (1.5295, 0.1000); Dispersant R.I. = 1.3300]
Analysis Model: Polydisperse — Residual: 0.485 %
Modifications: None

Result Statistics

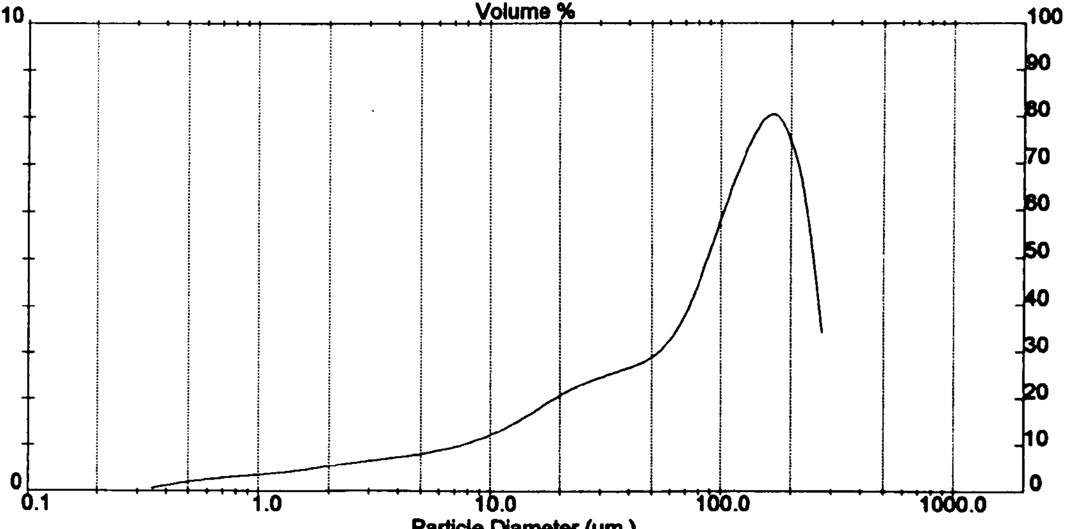
Distribution Type: Volume — Concentration = 0.1109 %Vol — Density = 1.000 g / cub. cm — Specific S.A. = 0.4609 sq. m / g
Span = 2.265E+00 — Uniformity = 7.238E-01

A.S.T.M Derived Diameters (um)				
N	3	2	1	0
D[4, N]	101.72	36.39	11.54	5.55
D[3, N]		13.02	3.89	2.11
D[2, N]			1.16	0.85
D[1, N]				0.62

Distribution Moments				
	Mean	Stan. Dev.	Skewness	Kurtosis
Volume	101.72	78.518	0.4754	-0.8359
Surface	13.02	33.982	4.2725	20.4403
Length	1.16	3.711	29.1230	1276.1099
Number	0.62	0.580	43.4904	8205.8311

Distribution Percentiles (um) – Volume			
Percentile	Size	Percentile	Size
10.0 %	7.28	80.0 %	176.73
20.0 %	20.43	90.0 %	216.07
50.0 %	92.18		

Distribution Modal Sizes (um)			
Mode	Size	Mode	Size
1	168.53		



MALVERN INSTRUMENTS MASTERSIZER

Result Derived Diameters Report

Sample Details

Sample ID: 95.4.34;1064;5.17
Sample File: (Result Not Saved)
Sample Path: A:\
Sample Notes:

Run Number: 3

Measured: Wed, Nov 04, 1998 11:14AM
Analysed: Wed, Nov 04, 1998 11:15AM
Result Source: Analysed

System Details

Range Lens: 100 mm
Presentation: 4OHD
Analysis Model: Polydisperse
Modifications: None

Beam Length: 2.40 mm
[Particle R.I. = (1.5295, 0.1000); Dispersant R.I. = 1.3300]

Sampler: None

Obscuration: 43.3 %
Residual: 0.571 %

Result Statistics

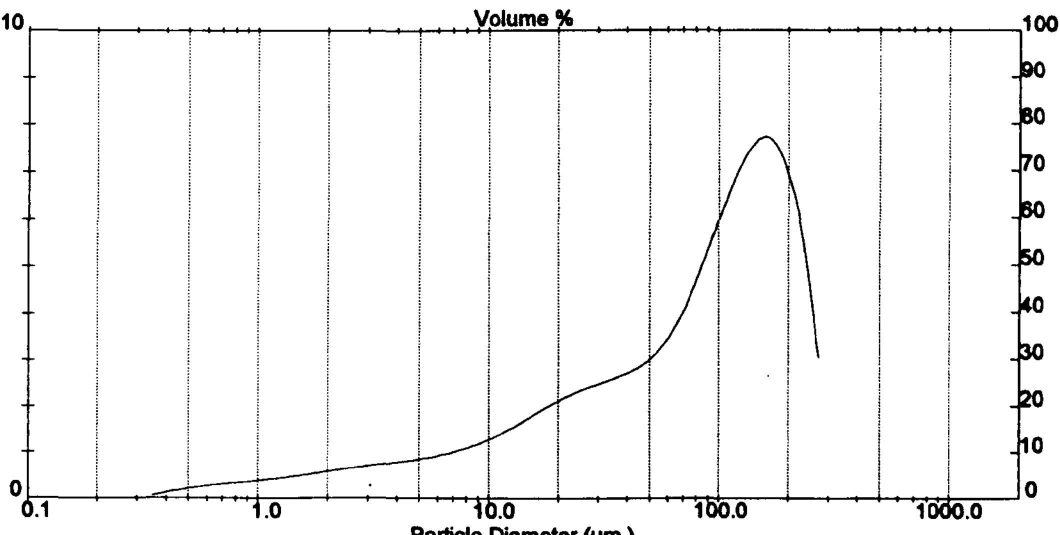
Distribution Type: Volume
Concentration = 0.1072 %Vol
Span = 2.342E+00
Density = 1.000 g / cub. cm
Uniformity = 7.471E-01
Specific S.A. = 0.4849 sq. m / g

A.S.T.M Derived Diameters (um)				
N	3	2	1	0
D[4, N]	97.99	34.82	11.19	5.43
D[3, N]		12.37	3.78	2.07
D[2, N]			1.16	0.85
D[1, N]				0.62

Distribution Moments				
	Mean	Stan. Dev.	Skewness	Kurtosis
Volume	97.99	77.116	0.5325	-0.7406
Surface	12.37	32.548	4.3844	21.7861
Length	1.16	3.602	29.0129	1281.1198
Number	0.62	0.577	41.7242	7654.4858

Distribution Percentiles (um) -- Volume			
Percentile	Size	Percentile	Size
10.0 %	6.65	80.0 %	170.72
20.0 %	19.02	90.0 %	210.86
50.0 %	87.21		

Distribution Modal Sizes (um)			
Mode	Size	Mode	Size
1	160.21		



MALVERN INSTRUMENTS MASTERSIZER

Result Derived Diameters Report

Sample Details

Sample ID: 95.4.34;3105;5.105
Sample File: (Result Not Saved)
Sample Path: A:\
Sample Notes:

Run Number: 4 1

Measured: Wed, Nov 04, 1998 9:59AM
Analysed: Wed, Nov 04, 1998 9:59AM
Result Source: Analysed

System Details

Range Lens: 100 mm
Presentation: 4OHD
Analysis Model: Polydisperse
Modifications: None

Beam Length: 2.40 mm
[Particle R.I. = (1.5295, 0.1000); Dispersant R.I. = 1.3300]

Sampler: None

Obscuration: 42.4 %
Residual: 3.291 %

Result Statistics

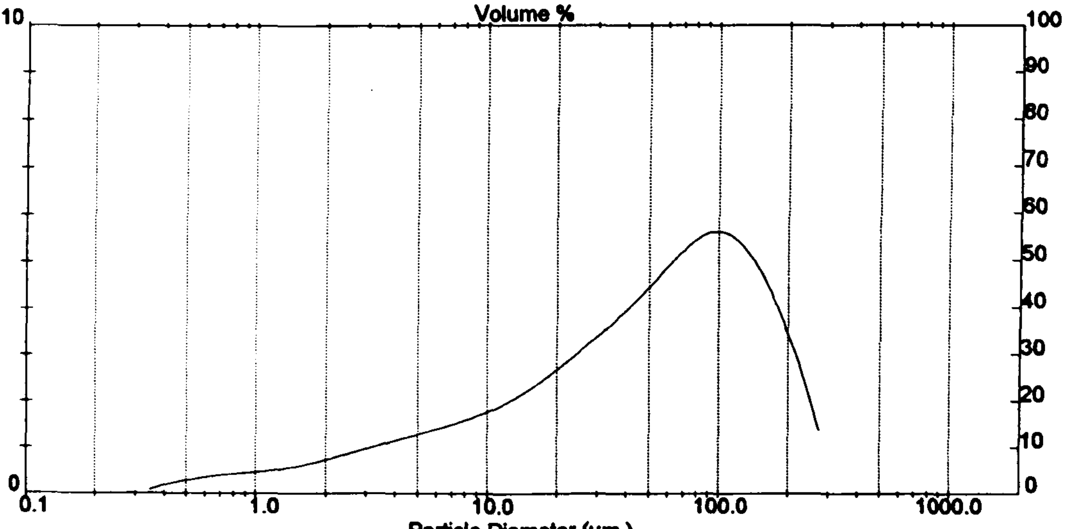
Distribution Type: Volume
Concentration = 0.0814 %Vol
Span = 3.164E+00
Density = 1.000 g / cub. cm
Uniformity = 9.792E-01
Specific S.A. = 0.6197 sq. m / g

A.S.T.M Derived Diameters (um)				
N	3	2	1	0
D[4, N]	71.13	26.24	9.26	4.70
D[3, N]		9.68	3.34	1.90
D[2, N]			1.15	0.84
D[1, N]				0.61

Distribution Moments				
	Mean	Stan. Dev.	Skewness	Kurtosis
Volume	71.13	65.700	1.0891	0.5451
Surface	9.68	24.390	5.0025	31.5779
Length	1.15	3.138	24.5851	1041.3004
Number	0.61	0.576	31.4985	4288.2524

Distribution Percentiles (um) -- Volume			
Percentile	Size	Percentile	Size
10.0 %	4.48	80.0 %	124.11
20.0 %	12.01	90.0 %	169.33
50.0 %	52.11		

Distribution Modal Sizes (um)			
Mode	Size	Mode	Size
1	98.64		



Result Derived Diameters Report

Sample Details		
Sample ID: 95.4.34;3105;5.105	Run Number: 2	Measured: Wed, Nov 04, 1998 11:46AM
Sample File: (Result Not Saved)		Analysed: Wed, Nov 04, 1998 11:46AM
Sample Path: A:\		Result Source: Analysed
Sample Notes:		

System Details			
Range Lens: 100 mm	Beam Length: 2.40 mm	Sampler: None	Obscuration: 46.8 %
Presentation: 4OHD	[Particle R.I. = (1.5295, 0.1000);	Dispersant R.I. = 1.3300]	
Analysis Model: Polydisperse			Residual: 0.457 %
Modifications: None			

Result Statistics			
Distribution Type: Volume	Concentration = 0.0931 %Vol	Density = 1.000 g / cub. cm	Specific S.A. = 0.6241 sq. m / g
	Span = 3.136E+00	Uniformity = 9.748E-01	

A.S.T.M Derived Diameters (um)

N	3	2	1	0
D[4, N]	72.32	26.37	9.23	4.68
D[3, N]		9.61	3.30	1.66
D[2, N]			1.13	0.83
D[1, N]				0.61

Distribution Moments

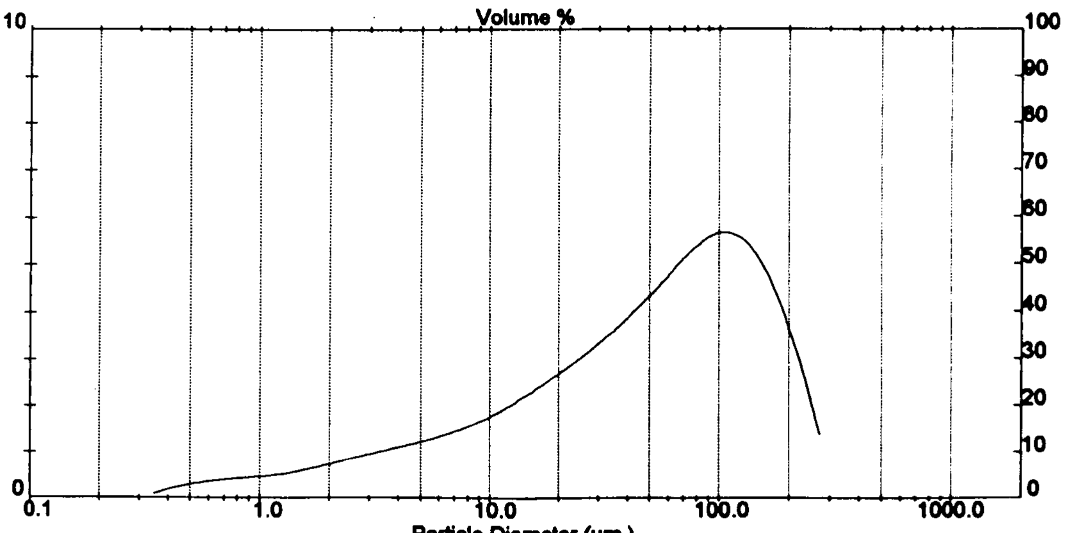
	Mean	Stan. Dev.	Skewness	Kurtosis
Volume	72.32	66.281	1.0445	0.4056
Surface	9.61	24.552	5.0159	31.4677
Length	1.13	3.096	25.3265	1096.8694
Number	0.61	0.563	32.4745	4595.5278

Distribution Percentiles (um) -- Volume

Percentile	Size	Percentile	Size
10.0 %	4.47	80.0 %	127.05
20.0 %	12.27	90.0 %	171.60
50.0 %	53.30		

Distribution Modal Sizes (um)

Mode	Size	Mode	Size
1	105.65		



MALVERN INSTRUMENTS **MASTERSIZER**

Result Derived Diameters Report

Sample Details

Sample ID: 95.4.34;3105;5.105
Sample File: (Result Not Saved)
Sample Path: A:\
Sample Notes:

Run Number: 3

Measured: Wed, Nov 04, 1998 11:50AM
Analysed: Wed, Nov 04, 1998 11:50AM
Result Source: Analysed

System Details

Range Lens: 100 mm
Presentation: 4OHD
Analysis Model: Polydisperse
Modifications: None

Beam Length: 2.40 mm
[Particle R.I. = (1.5295, 0.1000); Dispersant R.I. = 1.3300]

Sampler: None

Obscuration: 49.0 %
Residual: 0.436 %

Result Statistics

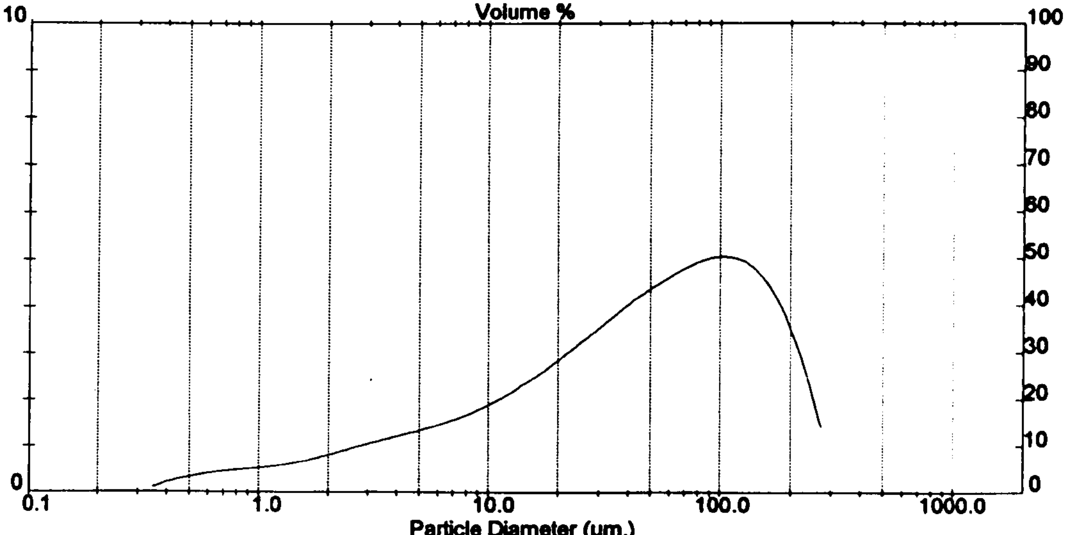
Distribution Type: Volume
Concentration = 0.0906 %Vol
Span = 3.527E+00
Density = 1.000 g / cub. cm
Uniformity = 1.083E+00
Specific S.A. = 0.6867 sq. m / g

A.S.T.M Derived Diameters (um)				
N	3	2	1	0
D[4, N]	68.96	24.55	8.74	4.48
D[3, N]		8.74	3.11	1.80
D[2, N]			1.11	0.82
D[1, N]				0.61

Distribution Moments				
	Mean	Stan. Dev.	Skewness	Kurtosis
Volume	68.96	66.501	1.1422	0.5962
Surface	8.74	22.939	5.4458	37.6316
Length	1.11	2.906	25.9745	1201.0797
Number	0.61	0.551	30.5059	4256.2759

Distribution Percentiles (um) – Volume			
Percentile	Size	Percentile	Size
10.0 %	3.88	80.0 %	122.97
20.0 %	10.57	90.0 %	170.41
50.0 %	47.21		

Distribution Modal Sizes (um)			
Mode	Size	Mode	Size
1	103.69		



Result Derived Diameters Report

Sample Details

Sample ID: 95.4.34;1059;5.15
Sample File: (Result Not Saved)
Sample Path: A:\
Sample Notes:

Run Number: 1

Measured: Wed, Nov 04, 1998 11:27AM
Analysed: Wed, Nov 04, 1998 11:27AM
Result Source: Analysed

System Details

Range Lens: 100 mm
Presentation: 4OHD
Analysis Model: Polydisperse
Modifications: None

Beam Length: 2.40 mm
[Particle R.I. = (1.5295, 0.1000); Dispersant R.I. = 1.3300]

Sampler: None

Obscuration: 39.8 %
Residual: 0.465 %

Result Statistics

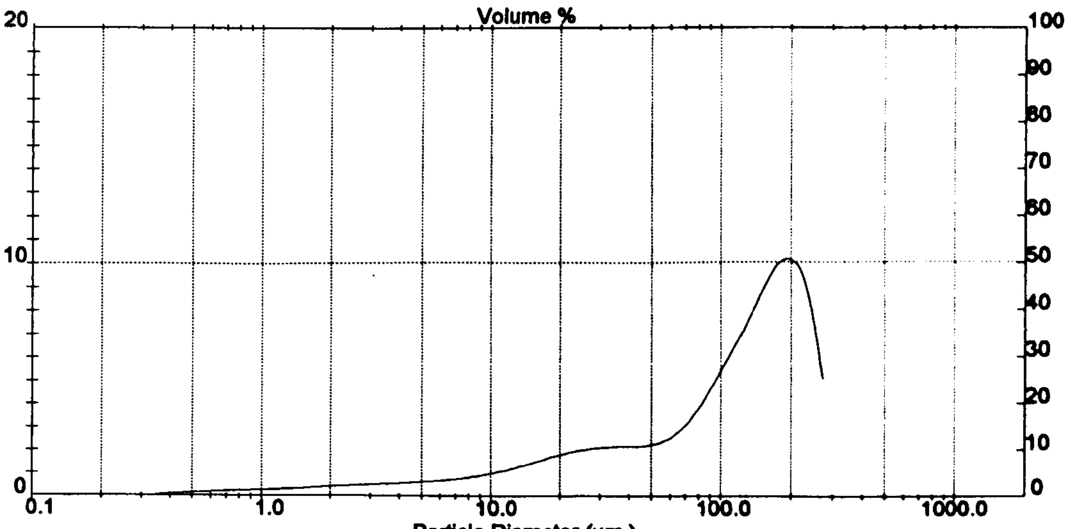
Distribution Type: Volume
Concentration = 0.1264 %Vol
Span = 1.875E+00
Density = 1.000 g / cub. cm
Uniformity = 5.974E-01
Specific S.A. = 0.3663 sq. m / g

A.S.T.M Derived Diameters (um)				
N	3	2	1	0
D[4, N]	119.38	44.22	13.29	6.17
D[3, N]		16.38	4.43	2.30
D[2, N]			1.20	0.86
D[1, N]				0.62

Distribution Moments				
	Mean	Stan. Dev.	Skewness	Kurtosis
Volume	119.38	82.178	0.1889	-1.0999
Surface	16.38	41.078	3.7048	14.4201
Length	1.20	4.267	29.3238	1208.4480
Number	0.62	0.599	52.1725	11001.1592

Distribution Percentiles (um) -- Volume			
Percentile	Size	Percentile	Size
10.0 %	10.79	80.0 %	199.38
20.0 %	28.08	90.0 %	233.00
50.0 %	118.53		

Distribution Modal Sizes (um)			
Mode	Size	Mode	Size
1	193.10		



MALVERN INSTRUMENTS MASTERSIZER

Result Derived Diameters Report

Sample Details

Sample ID: 95.4.34;1059;5.15
Sample File: (Result Not Saved)
Sample Path: A:\
Sample Notes:

Run Number: 2

Measured: Wed, Nov 04, 1998 11:30AM
Analysed: Wed, Nov 04, 1998 11:31AM
Result Source: Analysed

System Details

Range Lens: 100 mm
Presentation: 4OHD
Analysis Model: Polydisperse
Modifications: None

Beam Length: 2.40 mm
[Particle R.I. = (1.5295, 0.1000); Dispersant R.I. = 1.3300]

Sampler: None

Obscuration: 41.5 %
Residual: 0.539 %

Result Statistics

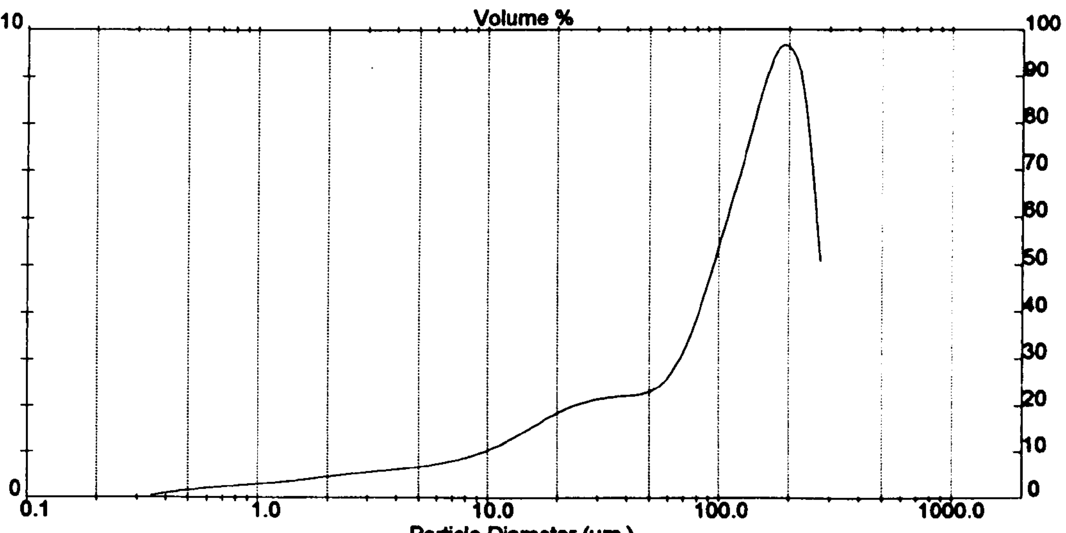
Distribution Type: Volume
Concentration = 0.1250 %Vol
Span = 1.954E+00
Density = 1.000 g / cub. cm
Uniformity = 6.238E-01
Specific S.A. = 0.3913 sq. m / g

A.S.T.M Derived Diameters (um)				
N	3	2	1	0
D[4, N]	116.71	42.30	12.86	6.02
D[3, N]		15.33	4.27	2.24
D[2, N]			1.19	0.86
D[1, N]				0.62

Distribution Moments				
	Mean	Stan. Dev.	Skewness	Kurtosis
Volume	116.71	82.660	0.2389	-1.0899
Surface	15.33	39.427	3.8918	16.1407
Length	1.19	4.098	29.9744	1281.7185
Number	0.62	0.593	49.7804	10417.4492

Distribution Percentiles (um) – Volume			
Percentile	Size	Percentile	Size
10.0 %	9.63	80.0 %	197.64
20.0 %	25.77	90.0 %	232.58
50.0 %	114.07		

Distribution Modal Sizes (um)			
Mode	Size	Mode	Size
1	192.78		



MALVERN INSTRUMENTS MASTERSIZER

Result Derived Diameters Report

Sample Details		
Sample ID: 95.4.34;1059;5.15	Run Number: 3	Measured: Wed, Nov 04, 1998 11:34AM
Sample File: (Result Not Saved)		Analysed: Wed, Nov 04, 1998 11:34AM
Sample Path: A:\		Result Source: Analysed
Sample Notes:		

System Details			
Range Lens: 100 mm	Beam Length: 2.40 mm	Sampler: None	Obscuration: 43.1 %
Presentation: 4OHD	[Particle R.I. = (1.5295, 0.1000);	Dispersant R.I. = 1.3300]	
Analysis Model: Polydisperse			Residual: 0.622 %
Modifications: None			

Result Statistics			
Distribution Type: Volume	Concentration = 0.1317 %Vol	Density = 1.000 g / cub. cm	Specific S.A. = 0.3913 sq. m / g
	Span = 1.922E+00	Uniformity = 6.127E-01	

A.S.T.M Derived Diameters (um)

N	3	2	1	0
D[4, N]	118.10	42.55	12.88	6.03
D[3, N]		15.33	4.25	2.24
D[2, N]			1.18	0.85
D[1, N]				0.62

Distribution Moments

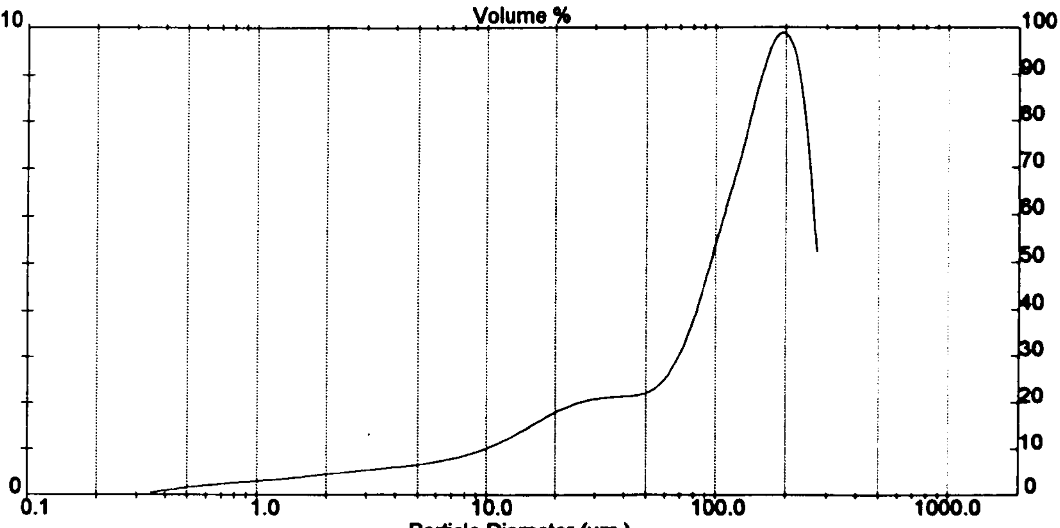
	Mean	Stan. Dev.	Skewness	Kurtosis
Volume	118.10	82.807	0.2125	-1.1005
Surface	15.33	39.696	3.8835	16.0019
Length	1.18	4.085	30.4264	1311.7166
Number	0.62	0.589	50.5094	10772.6367

Distribution Percentiles (um) – Volume

Percentile	Size	Percentile	Size
10.0 %	9.66	80.0 %	199.02
20.0 %	26.28	90.0 %	233.44
50.0 %	116.46		

Distribution Modal Sizes (um)

Mode	Size	Mode	Size
1	194.86		



MALVERN INSTRUMENTS MASTERSIZER

Result Derived Diameters Report

Sample Details

Sample ID: 95.4.34;2037;5.64 | Run Number: 1 | Measured: Wed, Nov 04, 1998 10:30AM
Sample File: (Result Not Saved) | Analysed: Wed, Nov 04, 1998 10:30AM
Sample Path: A:\ | Result Source: Analysed
Sample Notes:

System Details

Range Lens: 100 mm | Beam Length: 2.40 mm | Sampler: None | Obscuration: 41.9 %
Presentation: 4OHD | [Particle R.I. = (1.5295, 0.1000); Dispersant R.I. = 1.3300]
Analysis Model: Polydisperse | Residual: 0.441 %
Modifications: None

Result Statistics

Distribution Type: Volume | Concentration = 0.1462 %Vol | Density = 1.000 g / cub. cm | Specific S.A. = 0.3368 sq. m / g
Span = 2.107E+00 | Uniformity = 6.648E-01

A.S.T.M Derived Diameters (um)

N	3	2	1	0
D[4, N]	105.79	43.41	13.42	6.21
D[3, N]		17.81	4.78	2.41
D[2, N]			1.28	0.89
D[1, N]				0.62

Distribution Moments

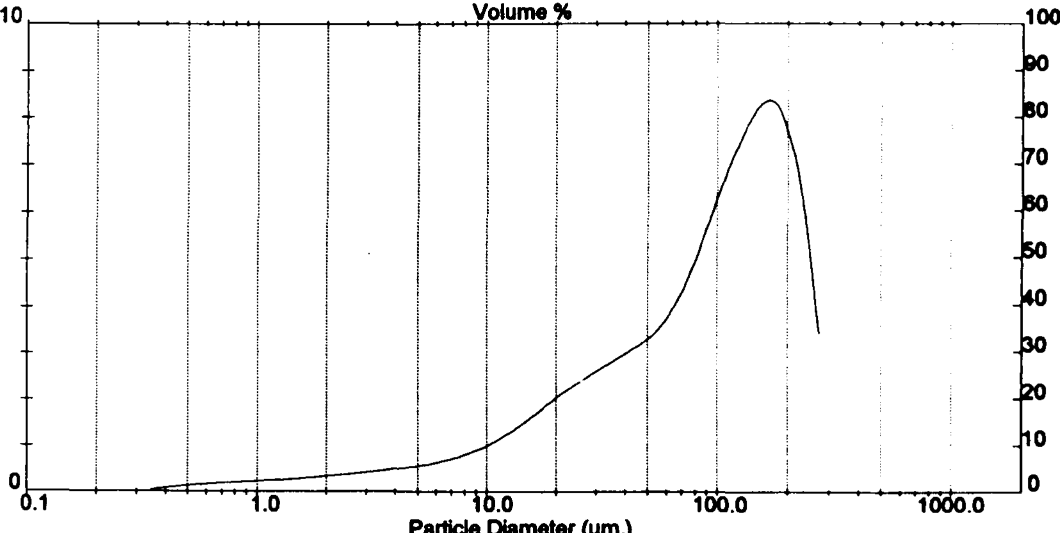
	Mean	Stan. Dev.	Skewness	Kurtosis
Volume	105.79	76.389	0.4518	-0.8027
Surface	17.81	39.588	3.4477	13.0178
Length	1.28	4.602	23.9100	836.0197
Number	0.62	0.640	49.8094	8655.0771

Distribution Percentiles (um) – Volume

Percentile	Size	Percentile	Size
10.0 %	12.38	80.0 %	178.16
20.0 %	27.77	90.0 %	216.51
50.0 %	96.87		

Distribution Modal Sizes (um)

Mode	Size	Mode	Size
1	168.98		



MALVERN INSTRUMENTS MASTERSIZER

Result Derived Diameters Report

Sample Details

Sample ID: 95.4.34;2037;5.64 | Run Number: 2 | Measured: Wed, Nov 04, 1998 10:33AM
Sample File: (Result Not Saved) | Analysed: Wed, Nov 04, 1998 10:34AM
Sample Path: A:\ | Result Source: Analysed
Sample Notes:

System Details

Range Lens: 100 mm | Beam Length: 2.40 mm | Sampler: None | Obscuration: 44.3 %
Presentation: 4OHD | [Particle R.I. = (1.5295, 0.1000); Dispersant R.I. = 1.3300]
Analysis Model: Polydisperse | Residual: 0.443 %
Modifications: None

Result Statistics

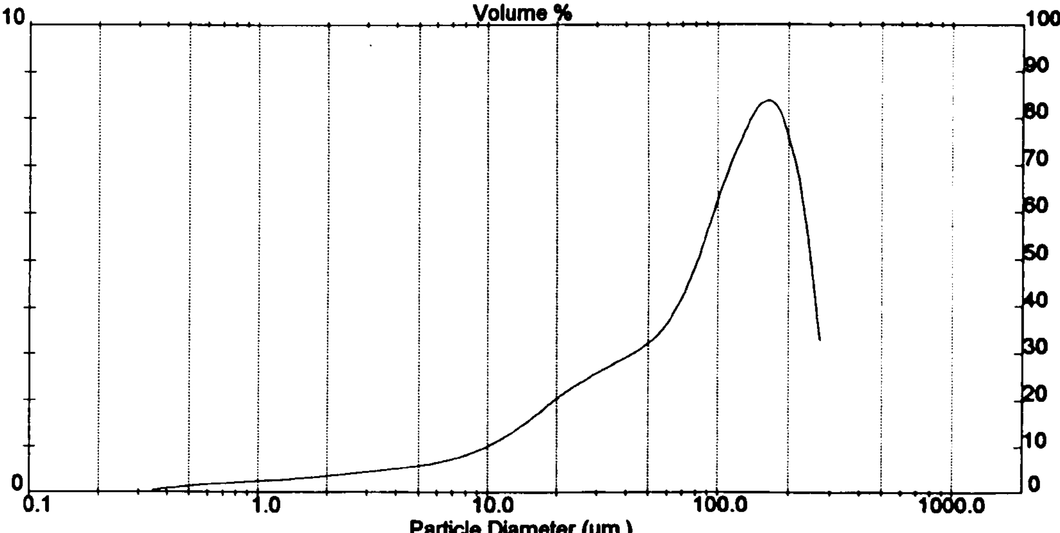
Distribution Type: Volume | Concentration = 0.1528 %Vol | Density = 1.000 g / cub. cm | Specific S.A. = 0.3473 sq. m / g
Span = 2.108E+00 | Uniformity = 6.654E-01

A.S.T.M Derived Diameters (um)				
N	3	2	1	0
D[4, N]	104.91	42.57	13.22	6.14
D[3, N]		17.28	4.69	2.39
D[2, N]			1.27	0.89
D[1, N]				0.62

Distribution Moments				
	Mean	Stan. Dev.	Skewness	Kurtosis
Volume	104.91	76.105	0.4551	-0.7893
Surface	17.28	38.911	3.5067	13.5031
Length	1.27	4.514	24.2199	859.0596
Number	0.62	0.636	48.9018	8492.9014

Distribution Percentiles (um) – Volume			
Percentile	Size	Percentile	Size
10.0 %	11.81	80.0 %	176.63
20.0 %	26.96	90.0 %	214.90
50.0 %	96.35		

Distribution Modal Sizes (um)			
Mode	Size	Mode	Size
1	166.01		



MALVERN INSTRUMENTS MASTERSIZER

Result Derived Diameters Report

Sample Details

Sample ID: 95.4.34;2037;5.64
Sample File: (Result Not Saved)
Sample Path: A:\
Sample Notes:

Run Number: 3

Measured: Wed, Nov 04, 1998 10:37AM
Analysed: Wed, Nov 04, 1998 10:37AM
Result Source: Analysed

System Details

Range Lens: 100 mm
Presentation: 4OHD
Analysis Model: Polydisperse
Modifications: None

Beam Length: 2.40 mm
[Particle R.I. = (1.5295, 0.1000); Dispersant R.I. = 1.3300]

Sampler: None

Obscuration: 45.8 %
Residual: 0.499 %

Result Statistics

Distribution Type: Volume
Concentration = 0.1632 %Vol
Span = 2.054E+00
Density = 1.000 g / cub. cm
Uniformity = 6.506E-01
Specific S.A. = 0.3418 sq. m / g

A.S.T.M Derived Diameters (um)

N	3	2	1	0
D[4, N]	109.25	43.79	13.40	6.20
D[3, N]		17.55	4.70	2.39
D[2, N]			1.26	0.88
D[1, N]				0.62

Distribution Moments

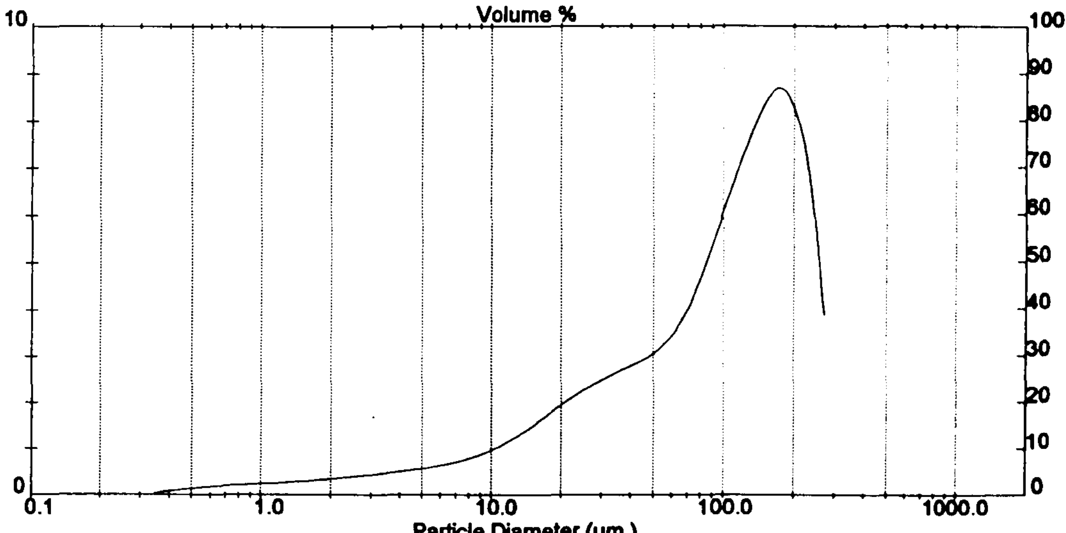
	Mean	Stan. Dev.	Skewness	Kurtosis
Volume	109.25	77.999	0.3920	-0.8880
Surface	17.55	40.119	3.5018	13.2915
Length	1.26	4.524	25.1541	916.7830
Number	0.62	0.628	50.9455	9331.3438

Distribution Percentiles (um) -- Volume

Percentile	Size	Percentile	Size
10.0 %	12.21	80.0 %	183.81
20.0 %	28.23	90.0 %	221.47
50.0 %	101.88		

Distribution Modal Sizes (um)

Mode	Size	Mode	Size
1	173.63		



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Mastersizer µ Ver. 2.12
Serial Number: 33031-20

APPENDIX FOUR: The data analysed using cluster analysis in Chapter 4.

An SPSS spreadsheet containing the data that were analysed to produce Dendrogram 4. 1.(and also Dendrograms 4. 6 and 4. 8. after removal of non-botanical and rare remains, respectively) is contained on Disc 1.

APPENDIX 5: Human use and ecological occurrence in modern-day Britain of the plant taxa in the cluster analysis of common seeds and grains.

Taxa are listed within clusters as they occur in Dendrogram 4. 1. Modern plant communities are listed as the volume numbers of Rodwell (where **1** covers woodlands and scrub, **2** covers mires and heaths, **3** covers grasslands and montane communities, **4** covers aquatic communities, swamps and tall-herb fens, and **5** covers maritime communities and vegetation of open habitats), and the letters and numbers following them in brackets are the codes for the individual plant communities. A list of the plant communities represented by the codes is found in Appendix 6.

A (i) (a) 1 Part One

Atriplex sp(p). = oraches

Human use	Modern plant communities
none	**2:** M28; **3:** MG11, MG12, MG13; **4:** S4, S18, S20, S21, S28; **5:** SD2, SD3, SD4, SD5, SD6, SM6, SM7, SM8, SM9, SM10, SM11, SM12, SM13, SM14, SM15, SM16, SM17, SM18, SM20, SM21, SM22, SM23, SM24, SM25, SM26, SM28, MC1, MC2, MC5, MC6, OV6, OV7, OV8, OV9, OV10, OV11, OV12, OV13, OV15, OV19, OV20, OV21, OV22, OV25, OV28, OV33.

Stellaria media = common chickweed

Human use	Modern plant communities
none	**1:** W2, W6, W10, W14, W21, W22; **2:** M28; **3:** MG3, MG7, MG11, MG12, U1; **4:** S21, S23; **5:** SD2, SD3, SD18, SM28, OV1, OV3, OV4, OV5, OV6, OV7, OV8, OV9, OV10, OV11, OV12, OV13, OV14, OV15, OV16, OV17, OV18, OV19, OV20, OV21, OV22, OV23, OV24, OV28, OV29, OV33, OV36.

Carex sp(p). = sedges

Human use	Modern plant communities
none	**1:** W1, W2, W3, W4, W5, W6, W7, W8, W9, W10, W11, W12, W14, W15, W17, W19, W20; **2:** M1, M2, M4, M5, M6, M7, M8, M9, M10, M11, M12, M13, M14, M15, M16, M17, M19, M20, M21, M22, M23, M24, M25, M26, M27, M29, M31, M32, M34, M35, M37, M38, H1, H3, H4, H5, H6, H7, H8, H9, H10, H11, H12, H13, H14, H15, H16, H17, H18, H19, H20, H21, H22; **3:** MG3, MG4, MG5, MG8, MG9, MG10, MG11, MG12, MG13, CG1, CG2, CG3, CG4, CG5, CG6, CG7, CG8, CG9, CG10, CG11, CG12, CG13, CG14, U1, U2, U3, U4, U5, U6, U7, U8, U9, U10, U11, U12, U13, U14, U15, U16, U17, U19, U20; **4:** A22, S1, S2, S3, S4, S5, S6, S7, S8, S9, S10, S11, S12, S14, S17, S18, S19, S20, S21, S22, S23, S24, S25, S26, S27; **5:** SM15, SM16, SM18, SM19, SM20, SM28, SD6, SD7, SD8, SD9, SD10, SD11, SD12, SD13, SD14, SD15, SD16, SD17, SD18, SD19, MC5, MC8, MC9, MC10, MC11, OV2, OV26, OV29, OV34, OV37, OV38, OV30, OV32.

Urtica dioica = common nettle

Human use	Modern plant communities
none	**1:** W2, W3, W5, W6, W7, W8, W9, W10, W12, W13, W14, W19, W21, W22, W24, W25; **2:** M27, M28, **3** MG1, MG2, MG9, MG10, MG11,CG2, CG4, CG6, U1; **4:** S3, S4, S5, S6, S7, S12, S14, S15, S23, S24, S25, S26, S28; **5:** SM28, SD6, SD12, SD18, OV3, OV8, OV9, OV10, OV12, OV13, OV15, OV17, OV19, OV21, OV23, OV24, OV25, OV26, OV27, OV28, OV33, OV41, OV42.

Ranunculus Section *Ranunculus* = buttercups

Human use	Modern plant communities

none	**1:** W1, W3, W5, W6, W7, W8, W9, W10, W11, W12, W14, W19, W20, W21, W24, W25; **2:** M5, M6, M8, M9, M10, M11, M12, M13, M22, M23, M24, M25, M26, M27, M28, M29, M31, M32, M34, M35, M38, H18; **3:** MG1, MG2, MG3, MG4, MG5, MG6, MG7, MG8, MG9, MG10, MG11,MG12, MG13, CG1, CG2, CG3, CG4, CG5, CG6, CG7, CG10, CG11, CG12, CG13, CG14, U4, U5, U13, U14, U15, U17, U20; **4:** A1, A2, A3, A4, A5, A6, A8, A9, A11, A12, A13, A14, A15, A17, A20, A21, A18, A19, S1, S4, S5, S7, S8, S9, S10, S11, S12, S13, S14, S15, S16, S17, S18, S19, S20, S21, S22, S23, S24, S26, S27, S28; **5:** SM16, SM18, SD6, SD7, SD8, SD9, SD12, SD14, SD15, SD16, SD17, OV2, OV4, OV5, OV6, OV7, OV9, OV10, OV11, OV12, OV15, OV19, OV20, OV21, OV22, OV23, OV25, OV26, OV28, OV29, OV30, OV31, OV32, OV33, OV35, OV36.

Chenopodium album = fat hen

Human use	Modern plant communities
none	**4:** S12, S23; **5:** OV3, OV5, OV6, OV7, OV8, OV9, OV10, OV11, OV12, OV13, OV14, OV15, OV16, OV17, OV18, OV19, OV22, OV24, OV28, OV33.

Polygonum aviculare = knotgrass

Human use	Modern plant communities
none	**3:** MG11; **4:** S7, S15, S23; **5:** OV3, OV4, OV5, OV6, OV7, OV8, OV9, OV10, OV11, OV12, OV13, OV14, OV15, OV16, OV17, OV18, OV19, OV20, OV21, OV28, OV29, OV31, OV33, OV36.

Rumex sp(p). = docks

Human use	Modern plant communities

none	1: W1, W4, W5,W6, W7, W8, W9, W10, W11, W12, W16, W17, W19, W20, W21, W22, W23, W24, W25; 2: M4, M5, M6, M12, M22, M23, M24, M25, M26, M27, M28, M32, M33, M37, H1, H7, H8, H9, H11, H18; 3: MG1, MG2, MG3, MG4, MG5, MG6, MG7, MG8, MG9, MG10, MG11, MG12, MG13, CG2, 3, 4, 6, 7, 10, 11, 12, U1, U2, U4, U7, U10, U13, U14, U15, U16, U17, U18, U19, U20, U21; 4: S1, S2, S3, S4, S5, S6, S7, S11, S12, S13, S14, S15, S17, S18, S20, S21, S22, S23, S24, S25, S26, S27; 5: SM18, SM28, SD1, SD2, SD3, SD4, SD5, SD6, SD7, SD8, SD9, SD10, SD11, SD13, SD14, SD17, MC2, MC3, MC4, MC6, MC8, MC9, MC10, MC11, MC12, OV1, OV2, OV3, OV4, OV5, OV6, OV8, OV9, OV10, OV11, OV13, OV14, OV17, OV18, OV19, OV20, OV21, OV22, OV23, OV25, OV26, OV27, OV29, OV31, OV32, OV33, OV36.

Sambucus nigra = elder

Human use	Modern plant communities
none	1: W6, W7, W8, W9, W10, W12, W13, W14, W21, W24, W25; 3: CG4, CG5, CG7; 5: SD18, OV27.

Urtica urens = small nettle

Human use	Modern plant communities
none	5: OV5, OV6, OV7, OV8, OV10, OV13, OV14, OV17, OV18, OV19.

Anthemis cotula = stinking chamomile

Human use	Modern plant communities
none	5: OV1, OV8, OV10, OV15, OV19, OV33, OV36.

Lapsana communis = nipplewort

Human use	Modern plant communities
none	1: W8, W24; 5: OV8, OV9, OV10, OV12, OV15, OV19, OV23, OV25.

Eleocharis palustris = common spike-rush

Human use	Modern plant communities
none	2: M22, M28, M29; 3: MG8; 4: A22, S4, S8, S9, S12, S14, S15, S19, S20, S21, S22, S23, S27, S28; 5: SD14, SD15, SD17, OV29, OV30, OV31, OV32, OV35.

Rumex acetosella = sheep's sorrel

Human use	Modern plant communities
none	**1:** W16, W23; **2:** H1, H8, H9, H11; **3:** CG7, U1, U2, U19, U20, U21; **5:** SD8, SD10, SD11, SD12, OV1, OV2, OV4, OV5, OV6, OV9, OV20.

Brassica rapa = turnip

Human use	Modern plant communities
food item	**5:** OV4, OV19.

Polygonum persicaria = redshank

Human use	Modern plant communities
none	**4:** S12, S14, S15, S19, S23; **5:** SD178, OV4, OV5, OV8, OV9, OV10, OV11, OV12, OV13, OV14, OV17, OV19, OV21, OV22, OV28, OV29, OV30, OV31, OV32, OV33, OV36.

Corylus avellana = hazel

Human use	Modern plant communities
food item	**1:** W1, W4, W6, W7, W8, W9, W10, W11, W12, W14, W16, W17, W21, W22, W24.

Galeopsis Subgenus *Galeopsis* = hemp nettles

Human use	Modern plant communities
none	**1:** W3, W6; **2:** M28; **5:** OV4, OV9, OV33.

Aethusa cynapium = fool's parsley

Human use	Modern plant communities
none	**5:** OV7, OV8, OV15, OV16.

Juncus bufonius = toad rush

Human use	Modern plant communities
none	**2:** M29, M35; **4:** S15, S18, S20, S21, S23; **3:** MG11, MG13; **5:** SM23, SD3, SD17, OV2, OV6, OV19, OV20, OV21, OV30, OV31, OV32, OV34, OV35, OV36.

Reseda luteola = weld

Human use	Modern plant communties
none	**3:** CG6

Rubus fruticosus = bramble

Human use	Modern plant communities
food item	**1:** W1, W2, W3, W4, W5, W6, W7, W8, W9, W10, W11, W12, W13, W14, W15, W16, W17, W21, W22, W23, W24, W25; **2:** M24, M25, M27, H2, H6, H8; **3:** MG1, MG9, U1, U2; **4:** S3, S4, S6, S17, S18, S24, S25, S26, S28; **5:** SD6, SD7, SD18, MC12, OV22, OV24, OV25, OV26, OV27.

Gramineae = indeterminate grasses
Too vague taxonomically to indicate the provenance of these plant remains.

Bilderdykia convolvulus = black bindweed

Human use	Modern plant communities
none	**3:** U1; **4:** S23; **5:** OV1, OV3, OV4, OV5, OV7, OV8, OV9, OV10, OV11, OV12, OV13, OV14, OV15, OV16, OV17, OV18, OV19, OV24, OV33, OV36.

Valerianella dentata = narrow-fruited cornsalad

Human use	Modern plant communtites
none	**5:** OV15, OV16.

Spergula arvensis = corn spurrey

Human use	Modern plant communities
none	**5:** OV1, OV2, OV3, OV4, OV5, OV6,OV10, OV11, OV13, OV14, OV17, OV19, OV22, OV23, OV33

Viola sp(p). = violets

Human use	Modern plant communities

none	**1:** W3, W4, W5, W7, W8, W9, W10, W11, W14, W17, W19, W20, W21, W22, W23, W24, W25; **2:** M4, M5, M6, M7, M8, M9, M11, M12, M13, M15, M22, M23, M24, M25, M27, M28, M29, M31, M32, M38, H3, H4, H6, H7, H8, H9, H10, H11, H12, H15, H16, H18, H20, H21; **3:** MG2, MG3, CG1, CG2, CG3, CG4, CG5, CG6, CG7, CG8, CG9, CG10, CG11, CG12, CG13, CG14, U1, U4, U5, U7, U10, U11, U13, U14, U15, U16, U17, U18, U19, U20; **4:** S1, S3, S21; **5:** SD7, SD8, SD9, SD11, SD12, SD14, SD16, SD19, MC9, MC10, MC12, OV1, OV3, OV4, OV5, OV6, OV7, OV9, OV10, OV11, OV12, OV16, OV21, OV27, OV33, OV36, OV37.

Hyoscyamus niger = henbane

Human use	Modern plant communities
none	maritime sand and shingle, inland rough and waste ground, especially manured.

Potentilla cf. erecta = ?tormentil

Human use	Modern plant communities
none	**1:** W2, W4, W9, W11, W16, W17, W18, W19, W23, W25; **2:** M4, M6, M8, M9, M10, M11, M12, M13, M14, M15, M16, M17, M19, M21, M22, M23, M24, M25, M26, M29, M38, H2, H3, H4, H5, H5, H6, H7, H8, H9, H10, H11, H12, H13, H14, H15, H16, H17, H18, H19, H20, H21, H22; **3:** MG2, MG3, MG5, MG9, CG2, CG9, CG10, CG11, CG12, CG13, CG14, U1, U2, U3, U4, U5, U6, U7, U10, U13, U14, U15, U16, U17, U19, U20, U21; **4:** S24; **5:** SD12, MC8, MC9, MC10, MC12, OV27.

Sonchus asper = prickly sow-thistle

Human use	Modern plant communities
none	**3:** MG1, MG11; **4:** S23; **5:** SD1, SD3, SD4, SD5, SD6, SD7, OV3, OV4, OV6, OV7, OV8, OV9, OV10, OV11, OV12, OV13, OV14, OV15, OV16, OV18, OV19, OV21, OV23, OV25, OV33, OV41, OV42.

Prunella vulgaris = selfheal

Human use	Modern plant communities

none	**1:** W6, W8, W9, W10, W11, W19, W24; **2:** M10, M11, M22, M23, M24, M26, M27, M32, M38, H7, H10; **3:** MG1, MG2, MG3, MG4, MG5, MG6, MG8, MG9, MG10, CG1, CG2, CG3, CG4, CG5, CG6, CG7, CG8, CG9, CG10, CG11, CG13, CG14, U4, U15, U19, U20; **5:** SD8, SD12, SD13, SD14, SD15, SD16, SD17, MC10, OV21, OV35.

Centaurea sp(p). = knapweeds

Human use	Modern plant communities
none	**1:** W24; **2:** M13, M22, M24, M25, M26, M27; **3:** MG1, MG2, MG3, MG4, MG5, MG6, MG8, MG9, CG1, CG2, CG3, CG4, CG5, CG6, CG7, CG7, CG8; **5:** SM28, SD7, SD8, SD9, SD15, MC4, MC9, MC11, OV23, OV24, OV25, OV38, OV39, OV41.

Chrysanthemum segetum = corn marigold

Human use	Modern plant communities
none	**5:** OV1, OV2, OV4, OV6, OV9, OV11.

Polygonum hydropiper = water pepper

Human use	Modern plant communities
none	**2:** M23, M27, M28; **3:** MG10, MG13; **4:** A17, S6, S7, S10, S23; **5:** OV21, OV28, OV29, OV30, OV31, OV32, OV35.

Polygonum lapathifolium = pale persicaria

Human use	Modern plant communities
none	**5:** OV4, OV7, OV11, OV13, OV21, OV26, OV29, OV31, OV32, OV33.

Brassica sp(p). = indeterminate members of the cabbage family

Human use	Modern plant communities
food items	?

Carduus/Cirsium sp(p). = thistles

Human use	Modern plant communities

none	**1:** W1, W2, W3, W4, W5, W6, W7, W9, W21, W24, W25; **2:** M5, M6, M8, M9, M10, M13, M16, M21, M22, M23, M24, M25, M26, M27, M28, M29, M38; **3:** MG1, MG2, MG3, MG4, MG5, MG6, MG7, MG8, MG9, MG10, MG11, MG12, MG13, CG1, CG2, CG3, CG4, CG5, CG6, CG7, CG8, CG9, U4, U5, U17, U19, U20; **4:** S1, S3, S5, S6, S7, S15, S17, S18, S21, S23, S24, S25, S26, S27, S28; **5:** OV25, SM18, SM28, SD1, SD2, SD4, SD5, SD6, SD7, SD8, SD9, SD12, SD15, SD16, SD18, SD19, MC4, MC5, MC8, MC11, MC12, OV3, OV4, OV5, OV7, OV8, OV9, OV10, OV13, OV14, OV15, OV16, OV19, OV20, OV21, OV22, OV23, OV25, OV26, OV27, OV28, OV29, OV31, OV32, OV33, OV37, OV41.

Prunus spinosa = blackthorn

Human use	Modern plant communities
none	**2:** H6; **1:** W6, W7, W8, W10, W21, W22, W24, W25.

Chenopodium Section *Pseudoblitum* = oak-leaved and red goosefoots

Human use	Modern plant communities
none	**4:** S20; **5:** OV13, OV31.

Ranunculus sceleratus = celery-leaved buttercup

Human use	Modern plant communities
none	**3:** MG13; **4:** A1, A20, S4, S12, S20, S21, S23; **5:** OV32.

Leontodon sp(p). = hawkbits

Human use	Modern plant communities
none	**2:** M8, M10, M11, M12, M13, M24, M26, M32, M38, H6, H7, H10; **3:** MG1, MG2, MG3, MG4, MG5, MG6, MG7, MG8, MG9, MG11, MG12, MG13, CG1, CG2, CG3, CG4, CG5, CG6, CG7, CG8, CG9, CG10, CG11, CG12, CG13, CG14, U1, U5, U14, U17; **4:** S19; **5:** SM16, SM18, SM19, SM20, SM28, SD1, SD7, SD8, SD9, SD13, SD14, SD15, SD16, SD17, SD18, MC2, MC3, MC5, MC8, MC9, MC10, MC11, OV11, OV21, OV34, OV38.

Ranunculus flammula = lesser spearwort

Human use	Modern plant communities

none	**1:** W1, W3, W5, W7; **2:** M5, M6, M9, M10, M11, M13, M22, M23, M24, M25, M27, M29, M31, M32, M35, M38; **3:** MG13; **4:** A22, S4, S8, S9, S10, S11, S12, S13, S14, S19, S21, S24, S27; **5:** SD14, SD15, SD16, SD17, MC10, OV30, OV31, OV35.

Silene vulgaris = bladder campion

Human use	Modern plant communities
none	**1:** W22; **2:** H7; **3:** MG11; **5:** OV16, OV17, 23, OV25.

Brassica sp./*Sinapis arvensis* = cabbage/mustard, etc.

Human use	Modern plant communities
food items	cultivated.

Malus sylvestris = crab apple

Human use	Modern plant communities
food items	Woods, hedges and scrub.

Agrostemma githago = corncockle

Human use	Modern plant communities
crop contaminant	Very rare, formerly a common cornfield weed.

A (i) (a) 1 Part Two

Menyanthes trifoliata = bogbean

Human use	modern plant communities
none	**1:** W2, W3, W4; **2:** M1, M2, M4, M5, M6, M9, M13, M15, M22, M25, M26, M29; **4:** S1, S2, S4, S8, S9, S10, S11, S12, S13, S24, S25, S27; **5:** OV26.

Ranunculus sardous = hairy buttercup

Human use	Modern plant communities
none	grassland and cultivated land.

Rubus idaeus = raspberry

Human use	Modern plant communities
food item	woods, heaths and marginal ground.

Conium maculatum = hemlock

Human use	Modern plant communities
none	**4:** S23; **5:** OV22, OV24, OV25.

A (i) (a) 2
Papaver argemone = prickly poppy

Human use	Modern plant communities
none	**5:** OV3.

Papaver somniferum = opium poppy

Human use	Modern plant communities
medicinal	cultivated.

Danthonia decumbens = heath grass

Human use	Modern plant communities
none	**2:** M13, M15, M16, M24, M25, H3, H4, H5, H6, H7, H8, H10, H12, H16, H18; **3:** MG5, MG9, CG1, CG2, CG3, CG4, CG5, CG6, CG8, CG9, CG10, CG11, CG13, CG14, U3, U4, U5, U20; **5:** SD12, SD14, SD15, MC9, MC10, OV34.

Plantago major = greater plantain

Human use	Modern plant communities
none	**3:** MG6, MG7, MG10, MG11, MG12, CG5; **4:** S18, S23; **5:** SD8, SD14, OV4, OV7, OV8, OV9, OV10, OV11, OV12, OV13, OV15, OV16, OV18, OV19, OV20, OV21, OV22, OV23, OV24, OV28, OV29, OV30, OV31, OV33, OV36.

Capsella bursa-pastoris = shepherd's purse

Human use	Modern plant communities
none	**5:** OV3, OV4, OV5, OV6, OV7, OV8, OV9, OV10, OV11, OV13, OV14, OV16, OV17, OV18, OV19, OV20, OV21, OV22, OV23, OV25, OV33.

A (i) (a) 3
Linum usitatissimum = flax

Human use	Modern plant communities
linen-making	cultivated.

Malus sp(p). = apples

Human use	Modern plant communities

food items	Cultivated. Also **1:** W8, W10, W21.

Prunus domestica ssp. *insititia* = bullace/damson

Human use	Modern plant communities
food items	Cultivated? Hedges, copses, scrub and waste ground.

Prunus section *cerasus* = dwarf cherry

Human use	Modern plant communities
food item	Cultivated? Hedges and copses.

Avena sp(p). (w/l) = waterlogged oats

Human use	Modern plant communities
food item	cultivated.

A (i) (b)
Fumaria sp(p). = fumitory

Human use	Modern plant communities
none	**5:** OV4, OV6, OV9, OV10, OV11, OV13, OV14, OV15, OV16, OV18, OV24, OV33.

Lamium Section *Lamiopsis* = dead nettles

Human use	Modern plant communities
none	**1:** W21; **3:** MG1; **5:** OV4, OV6, OV7, OV8, OV9, OV10, OV11, OV12, OV13, OV14, OV18, OV19, OV22, OV25.

A (i) (c)
Foeniculum vulgare = fennel

Human use	Modern plant communities
food item	cultivated, open and waste ground.

Vitis vinifera = vine (grapes)

Human use	modern plant communities
food item	generally imported crop

Ficus carica = fig

Human use	Modern plant communities
food item	imported crop

Fragaria cf. vesca = wild (?) strawberry

Human use	Modern plant communities
food item	cultivated.

A (i) (d)

Anagallis arvensis = scarlet pimpernel

Human use	Modern plant communities
none	**5:** OV1, OV2, OV3, OV4, OV5, OV6, OV7, OV9, OV10, OV11, OV12, OV15, OV16, OV17, OV18, OV19, OV21, OV28, OV33, OV36.

Umbelliferae = indeterminate members of the carrot family
Too vague to allow provenance identification.

Avena sp(p). = charred oats

Human use	Modern plant communities
food item	cultivated.

Hordeum sp(p). = charred barley

Human use	Modern plant communities
food item	cultivated.

Alisma sp(p). = water plantain

Human use	Modern plant communities
none	**4:** A2, A4, A9, A20, S5, S8, S10, S12, S13, S14, S15, S17, S18, S19, S22; **5:** OV30, OV31, OV35.

Juncus inflexus/effusus/conglomeratus = hard/soft/compact rushes

Human use	Modern plant communities
none	**1:** W1, W2, W3, W4, W5, W6, W7, W8, W10, W21; **2:** M4, M5, M6, M8, M15, M16, M21, M22, M23, M24, M25, M26, M27, M28, M29, M32, M35; **3:** MG5, MG6, MG8, MG9, MG10, MG13, U2, U4, U5, U19; **4:** S4, S5, S6, S7, S8, S9, S11, S12, S13, S14, S15, S17, S18, S19, S23, S26, S27, S28; **5:** SD14, SD15, SD16, SD17, OV26, OV27, OV28, OV30, OV32, OV35.

Linum catharticum = fairy flax

Human use	Modern plant communities

linen making?	**2:** M8, M10, M11, M13, M24, M38, H5, H8, H10; **3:** MG1, CG1, CG2, CG3, CG4, CG5, CG6, CG7, CG8, CG9, CG10, CG11, CG12, CG13, CG14, U15, U17; **5:** SD7, SD8, SD14, SD15, SD16, SD17, MC10, OV37.

Potentilla anserina = silverweed

Human use	Modern plant communities
none	**2:** M22, M23, M24, M27, M28; **3:** MG6, MG9, MG10, MG11, MG12, MG13; **4:** S19, S20, S21, S23, S26; **5:** SM16, SM18, SM19, SM20, SM24, SM28, SD1, SD2, SD8, SD10, SD14, SD15, SD16, SD17, OV4, OV9, OV11, OV21, OV26, OV28, OV29, OV30, OV31, OV32.

Potentilla cf. reptans = creeping (?) cinquefoil

Human use	Modern plant communities
none	**2:** M22, M24, M27; **3:** MG1, MG5, MG6, MG11, CG3, CG6, CG7, U1; **4:** S18; **5:** SD9, SD15, MC4, MC11, OV19, OV22, OV23, OV24, OV25.

A (i) (e)

Caltha palustris = marsh marigold

Human use	Modern plant communities
none	**2:** M5, M8, M9, M10, M11, M12, M13, M22, M23, M26, M27, M28, M32, M37, M38; **3:** MG3, MG4, MG8, MG10, MG13; **4:** S1, S2, S3, S7, S8, S9, S10, S11, S12, S17, S19, S21, S23, S24, S25, S27; **5:** SD15, SD17, OV26, OV29.

Rhinanthus sp(p). = yellow rattle

Human use	Modern plant communities
none	**1:** W20; **2:** M22, M26; **3:** MG1, MG3, MG4, MG5, MG6, MG8, CG1, CG2, CG3, CG5, CG8, CG14, U15, U17; **4:** S24; **5:** SD7, SD8, SD14, SD16, SD17.

Agrostis sp(p). = bents

Human use	Modern plant communities

none	**1:** W1, W2, W3, W4, W5, W6, W7, W9, W10, W11, W14, W15, W16, W17, W18, W19, W20, W22, W23, W24, W25; **2:** M2, M3, M4, M5, M6, M7, M8, M11, M12, M13, M15, M16, M17, M21, M22, M23, M24, M25, M26, M27, M28, M29, M31, M32, M33, M35, M37, M38, H1, H2, H3, H4, H5, H6, H7, H8, H9, H10, H11, H12, H13, H14, H15, H16, H17, H18, H19, H20, H21; **4:** S1, S4, S6, S8, S9, S11, S12, S13, S14, S17, S18, S19, S20, S21, S22, S23, S24, S26, S27, S28; **5:** SM13, SM15, SM16, SM17, SM18, SM19, SM20, SM23, SM24, SM28, SD2, SD3, SD4, SD6, SD7, SD8, SD9, SD10, SD11, SD12, SD13, SD14, SD15, SD16, SD17, SD18, MC2, MC3, MC4, MC5, MC8, MC9, MC10, MC11, OV1, OV3, OV4, OV6, OV7, OV9, OV10, OV11, OV12, OV13, OV14, OV15, OV16, OV17, OV18, OV19, OV20, OV21, OV22, OV23, OV24, OV25, OV26, OV27, OV28, OV29, OV30, OV31, OV32, OV33, OV34, OV35, OV37, OV42.

Bromus sp(p). (w/l) = waterlogged bromes

Human use	Modern plant communities
none	**1:** W8, W9, W10, W12, W14, W21, W24; **3:** MG1, MG2, MG3, MG4, MG5, MG6, MG7, MG8, MG11, MG13, CG1, CG2, CG3, CG5, CG8, U1; **5:** MC4, MC5, MC6, MC11, OV1, OV2, OV9, OV10, OV13, OV16, OV17, OV19, OV21, OV22, OV23, OV24, OV25, OV41.

Cerastium sp(p). = mouse-ears

Human use	Modern plant communities
none	**1:** W11, W19, W23, W24; **2:** M8, M11, M12, M22, M23, M24, M31, M32, M33, M37, M38, H1, H7, H11, H18; **3:** MG1, MG2, MG3, MG4, MG5, MG6, MG7, MG8, MG9, MG10, MG11, MG12, CG1, CG2, CG3, CG4, CG5, CG6, CG7, CG8, CG9, CG10, CG11, CG12, CG13, CG14, U1, U2, U3, U4, U5, U6, U7, U8, U9, U10, U11, U12, U13, U14, U15, U16, U17, U18, U19; **5:** SM16, SD1, SD2, SD4, SD6, SD7, SD8, SD9, SD10, SD12, SD13, SD16, SD17, SD18, SD19, MC1, MC2, MC5, MC8, MC9, MC10, OV2, OV4, OV6, OV9, OV10, OV11, OV12, OV15, OV19, OV21, OV22, OV23, OV24, OV25, OV26, OV27, OV28, OV37, OV41, OV42.

Centaurea sp(p). (min) = mineralised knapweeds

Human use	Modern plant communities
none	**1:** W24; **2:** M13, M22, M24, M25, M26, M27; **3:** MG1, MG2, MG3, MG4, MG5, MG6, MG8, MG9, CG1, CG2, CG3, CG4, CG5, CG6, CG7, CG8; **5:** SM28, SD7, SD8, SD9, SD15, SD17, MC4, MC9, MC11, OV23, OV24, OV25, OV38, OV39, OV41.

Gramineae (min) = mineralised indeterminate members of the grass family
Too general taxonomically to indicate provenance.

A (i) (f)
Anthriscus sylvestris = cow parsley

Human use	Modern plant communities
none	**1:** W8, W9, W10, W12, W24; **3:** MG1, MG2, MG3; **4:** S17; **5:** SM28, OV24, OV25, OV26, OV27.

Heracleum sphondylium = hogweed

Human use	Modern plant communities
none	**1:** W6, W8, W9, W10, W12, W21, W24, W25; **2:** M27, **3** MG1, MG2, MG3, MG4, MG5, MG9, MG14, MG17; **4:** S23, S26; **5:** SM28, SD6, SD7, SD8, SD9, SD18, MC9, MC12, OV3, OV6, OV10, OV12, OV15, OV18, OV19, OV21, OV22, OV23, OV24, OV25, OV26, OV27.

Galeopsis Subgenus *ladanum* = broad-leaved hemp nettle

Human use	Modern plant communities
none	? sporadic today.

Silene alba = white campion

Human use	Modern plant communities
none	**5:** SD9, OV3, OV15, OV16, OV17, OV18, OV19, OV22, OV24.

Anthemis cotula = stinking chamomile

Human use	Modern plant communities
none	**5:** OV1, OV8, OV10, OV15, OV19, OV33, OV36.

Pedicularis palustris = marsh lousewort

Human use	Modern plant communities
none	**2:** M8, M9, M10, M13, M15, M22, M29; **4:** S9, S24, S25; **5:** SD17.

Soncus oleraceus = smooth sow-thistle

Human use	Modern plant communities
none	**5:** SD8, MC4, MC5, MC6, MC8, MC11, MC12, OV2, OV3, OV6, OV7, OV8, OV10, OV13, OV14, OV19, OV22, OV23, OV25, OV36.

A (ii)

Rubia tinctorum = madder

Human use	Modern plant communities
dye plant	no longer occurs in Britain.

Triticum aetivo-compactum = charred wheat

Human use	Modern plant communities
food item	crop.

B

Bupleurum rotundifolium = thorow-wax

Human use	Modern plant communities
none	extinct in Britain since 1960s, formerly common in cornfields.

Torilis japonica = upright hedge parsley

Human use	Modern plant communities
none	**1:** W21; **3:** MG12; **5** SM28, SD9, OV23.

Cerealia indet. = indeterminate charred cereals

Human use	Modern plant communities
food item	crop.

Chrysanthemum segetum (ch.) = charred corn marigold

Human use	Modern plant communities
none	**5:** OV1, OV2, OV4, OV6, OV9, OV11.

C

Arctium sp(p). = burdock

Human use	Modern plant communities
none	**1:** W8, W12, W21; **3:** CG3, CG7; **5:** OV10, OV13, OV24, OV25, OV32.

Potentilla sp(p). = cinquefoils

Human use	Modern plant communities
none	**1:** W1, W2, W3, W4, W9, W11, W16, W17, W18, W19, W23, W25; **2:** M4, M5, M6, M8, M9, M10, M11, M12, M13, M14, M15, M16, M17, M19, M21, M22, M23, M24, M25, M26, M27, M28, M29, M38, H2, H3, H4, H5, H6, H7, H8, H9, H10, H11, H12, H13, H14, H15, H16, H17, H18, H19, H20, H21, H22; **3:** MG1, MG2, MG3, MG4, MG5, MG6, MG9, MG10, MG11, MG12, MG13, CG1, CG2, CG3, CG6, CG7, CG9, CG10, CG11, CG12, CG13, CG14, U1, U2, U3, U4, U5, U6, U7, U10, U13, U14, U15, U16, U17, U19, U20, U21; **4:** A4, S1, S2, S3, S4, S8, S9, S10, S11, S12, S18, S19, S20, S21, S23, S24, S25, S26, S27; **5:** SM16, SM18, SM19, SM20, SM24, SM28, SD1, SD2, SD8, SD9, SD10, SD12, SD14, SD15, SD16, SD17, MC4, MC8, MC9, MC10, MC11, MC12, OV4, OV9, OV11, OV19, OV21, OV22, OV23, OV24, OV25, OV26, OV27, OV28, OV29, OV30, OV31, OV32, OV39.

D

Fragaria vesca = strawberry

Human use	Modern plant communities
food item	crop.

Vaccinium sp(p). = bilberry/blueberry

Human use	Modern plant communities
food item	crop.

Centaurea cyanus = cornflower

Human use	Modern plant communities
none	cereal fields.

Juncus sp(p). = rushes

Human use	Modern plant communities

none	1: W1, W2, W3, W4, W5, W6, W7, W8, W10, W21; 2: M1, M4, M5, M6, M7, M8, M9, M10, M11, M12, M13, M14, M15, M16, M17, M18, M19, M20, M21, M22, M23, M24, M25, M26, M27, M28, M29, M30, M31, M32, M34, M35, M37, M38, H4, H5, H9, H10, H12, H13, H14, H16, H17, H18, H19, H20, H22; 3: MG5, MG6, MG7, MG8, MG9, MG10, MG11, MG12, MG13, CG10, CG11, CG12, U2, U4, U5, U6, U7, U8, U9, U10, U11, U12, U14, U15, U16, U18, U19; 4: A7, A8, A9, A10, A11, A13, A14, A22, A23, A24, A27, A28; 5: SM13, SM14, SM15, SM17, SM18, SM19, SM20, SM23, SM24, SM28, SD3, SD13, SD14, SD15, SD16, SD17, OV2, OV6, OV9, OV19, OV20, OV21, OV26, OV27, OV28, OV29, OV30, OV31, OV32, OV34, OV35, OV36, MC10.

Mentha sp(p). = mint

Human use	Modern plant communities
food item	cultivated and **1:** W1, W2, W3, W5, W6, W7; **2:** M5, M9, M13, M22, M23, M24, M25, M27, M28; **3:** MG8, MG9, MG10, MG13; **4:** A1, A8, A18, S1, S2, S3, S4, S5, S6, S7, S8, S9, S11, S12, S13, S14, S15, S17, S19, S21, S22, S23, S27, S28; **5:** SD13, SD14, SD15, SD16, SD17, OV15, OV26, OV28, OV30, OV31, OV32, OV35, OV36.

E

Prunus domestica ssp. *domestica* = plum

Human use	Modern plant communities
food item	Cultivated. Hedges, copses, scrub and waste ground.

Satureja hortensis = summer savory

Human use	Modern plant communities
none	? No modern references for Britain.

Prunus sp(p). = plum/sloe/cherry, etc.

Human use	Modern plant communities
food item	crop.

Cannabis sativa = hemp

Human use	Modern plant communities

fibres used for rope. Also medicinal?	cultivated.

Montia fontana ssp. *chondrosperma* = blinks

Human use	Modern plant communities
none	**2:** M4, M28, M32, M33, M35, M37; **5:** OV2.

Corylus avellana (ch.) = charred hazel

Human use	Modern plant communities
food item	**1:** W1, W4, W6, W7, W8, W9, W10, W11, W12, W14, W16, W17, W21, W22, W24.

F

Agrostemma githago (min) = mineralised corncockle

Human use	Modern plant communities
crop contaminant	Very rare today, formerly common in cornfields.

Avena spp. (min) = mineralised oats

Human use	Modern plant communities
food item	Cultivated.

Pisum sp(p). (min) = mineralised peas

Human use	Modern plant communities
food item	Cultivated. Also by road, fields, in waste places and on tips.

APPENDIX 6: Full names of the modern British plant communities in which the taxa included in cluster analysis of common seeds and grains occur (according to Rodwell, 1996-2000).

Volume One (Woodlands and scrub):

W1 = *Salix cinerea-Galium palustre* woodland
W2 = *Salix cinerea-Betula pubescens-Phragmites australis* woodland
W3 = *Salix pentandra-Carex rostrata* woodland
W4 = *Betula pubescens-Molinia caerulea* woodland
W5 = *Alnus glutinosa-Carex paniculata* woodland
W6 = *Alnus glutinosa-Urtica dioica* woodland
W7 = *Alnus glutinosa-Fraxinus excelsior-Lysimachia nemorum* woodland
W8 = *Fraxinus excelsior-Acer campestre-Mercurialis perennis* woodland
W9 = *Fraxinus excelsior-Sorbus aucuparia-Mercurialis perennis* woodland
W10 = *Quercus robur-Pteridium aquilinum-Rubus fruticosus* woodland
W11 = *Quercus petraea-Betula pubescens-Oxalis acetosella* woodland
W12 = *Fagus sylvatica-Mercurialis perennis* woodland
W13 = *Taxus baccata* woodland
W14 = *Fagus sylvatica-Rubus fruticosus* woodland
W15 = *Fagus sylvatica-Deschampsia flexuosa* woodland
W16 = *Quercus* spp.-*Betula* spp.-*Deschampsia flexuosa* woodland
W17 = *Quercus petraea-Betula pubescens-Dicranum majus* woodland
W18 = *Pinus sylvestris-Hylocomium splendens* woodland
W19 = *Juniperus communis* ssp. *communis-Oxalis acetosella* woodland
W20 = *Salix lapponum-Luzula sylvatica* scrub
W21 = *Crataegus monogyna-Hedera helix* scrub
W22 = *Prunus spinosa-Rubus fruticosus* scrub
W23 = *Ulex europaeus-Rubus fruticosus* scrub
W24 = *Rubus fruticosus-Holcus lanatus* scrub
W25 = *Pteridium aquilinum-Rubus fruticosus* underscrub

Volume Two (Mires and heaths):

M1 = *Sphagnum auriculatum* bog pool community
M2 = *Sphagnum cuspidatum/recurvum* bog pool community
M3 = *Eriophorum angustifolium* bog pool community
M4 = *Carex rostrata-Sphagnum recurvum* mire
M5 = *Carex rostrata-Sphagnum squarrosum* mire
M6 = *Carex echinata-Sphagnum recurvum/auriculatum* mire
M7 = *Carex curta-Sphagnum russowii* mire
M8 = *Carex rostrata-Sphagnum warnstorfii* mire
M9 = *Carex rostrata-Calliergon cuspidatum/giganteum* mire
M10 = *Pinguiculo-Caricetum dioicae* mire
M11 = *Carici-Saxifragetum aizoidis* mire
M12 = *Caricetum saxatilis* mire
M13 = *Schoenetum nigricantis* mire
M14 = *Schoenus nigricans-Narthecium ossifragum* mire
M15 = *Scirpus cespitosus-Erica tetralix* wet heath
M16 = *Ericetum tetralicis* wet heath
M17 = *Scirpus cespitosus-Eriophorum vaginatum* blanket mire
M19 = *Calluna vulgaris-Eriophorum vaginatum* blanket mire
M20 = *Eriophorum vaginatum* blanket and raised mire
M21 = *Narthecio-Sphagnetum* valley mire
M22 = *Juncus subnodulosus-Cirsium palustre* fen-meadow
M23 = *Juncus effusus/acutiflorus-Galium palustre* rush-pasture
M24 = *Cirsio-Molinietum caeruleae* fen-meadow

M25 = *Molinia caerulea-Potentilla erects* mire
M26 = *Molinia caerulea-Crepis paludosa* mire
M27 = *Filipendula ulmaria-Angelica sylvestris* mire
M28 = *Filipendulo-Iridetum* mire
M29 = *Hyperico-Potametum polygonifolii* soakway
M30 = Related vegetation of seasonally inundated habitats
M31 = *Sphagno-Anthelietum julaceae* spring
M32 = *Philonoto-Saxifragetum stellaris* spring
M33 = *Pohlietum glacialis* spring
M34 = *Carex demissa-Koenigia islandica* flush
M35 = *Ranunculus omiophyllus-Montia fontana* rill
M37 = *Cratoneuron commutatum-Festuca rubra* spring
M38 = *Cratoneuron commutatum-Carex nigra* spring
H1 = *Calluna vulgaris-Festuca ovina* heath
H2 = *Calluna vulgaris-Ulex minor* heath
H3 = *Ulex minor-Agrostis curtisii* heath
H4 = *Ulex gallii-Agrostis curtisii* heath
H5 = *Erica vagans-Schoenus nigricans* heath
H6 = *Erica vagans-Ulex europaeus* heath
H7 = *Calluna vulgaris-Scilla verna* heath
H8 = *Calluna vulgaris-Ulex gallii* heath
H9 = *Calluna vulgaris-Deschampsia flexuosa* heath
H10 = *Calluna vulgaris-Erica cinerea* heath
H11 = *Calluna vulgaris-Carex arenaria* heath
H12 = *Calluna vulgaris-Vaccimium myrtillus* heath
H13 = *Calluna vulgaris-Cladonia arbuscula* heath
H14 = *Calluna vulgaris-Racomitrium lanuginosum* heath
H15 = *Calluna vulgaris-Juniperus comunis* ssp. *nana* heath
H16 = *Calluna vulgaris-Arctostaphylos uva-ursi* heath
H17 = *Calluna vulgaris--Arctostaphylos alpinus* heath
H18 = *Vaccinium myrtillus-Deschampsia flexuosa* heath
H19 = *Vaccinium myrtillus- Cladonia arbuscula* heath
H20 = *Vaccinium myrtillus-Racomitrium lanuginosum* heath
H21 = *Calluna vulgaris-Vaccinium myrtillus-Sphagnum capillifolium* heath
H22 = *Vaccinium myrtillus-Rubus chamaemorus* heath

Volume Three (Grasslands and montane communities):
MG1 = *Arrhenatheretum elatioris* grassland
MG2 = *Filipendulo-Arrhenatheretum* tall-herb grassland
MG3 = *Anthoxanthum odoratum-Geranium sylvaticum* grassland
MG4 = *Alopecuris pratensis-Sanguisorba officinalis* grassland
MG5 = *Centaureo-Cynosuretum cristati* grassland
MG6 = *Lolio-Cynosuretum cristati* grassland
MG7 = *Lolio-Plantaginion* leys and related grasslands
MG8 = *Cynosurus cristatus -Caltha palustris* grassland
MG9 = *Holcus lanatus-Deschampsia cespitosa* grassland
MG10 = *Holco-Juncetum effusi* rush-pasture
MG11 = *Festuca rubra-Agrostis stolonifera-Potentilla anserina* grassland
MG12 = *Potentillo-Festucetum arundinaceae* grassland
MG13 = *Agrostis stolonifera-Alopecurus geniculatus* grassland
MG14 = ?
MG17 = **?**
CG1 = *Festuca ovina-Carlina vulgaris* grassland
CG2 = *Festuca ovina-Avenula pratensis* grassland
CG3 = *Bromus erectus* grassland
CG4 = *Brachypodium pinnatum* grassland
CG5 = *Bromus erectus-Brachypodium pinnatum* grassland
CG6 = *Avenula pubescens* grassland

CG7 = *Festuca ovinia-Hieracium pilosella-Thymus praecox/pulegioides* grassland
CG8 = *Sesleria albicans-Scabiosa columbaria* grassland
CG9 = *Sesleria albicans-Galium sterneri* grassland
CG10 = *Festuca ovinia-Agrostis capillaris-Thymus praecox* grassland
CG11 = *Festuca ovina-Agrostis capillaris-Alchemilla alpina* grass-heath
CG12 = *Festuca ovina-Alchemilla alpina-Silene acaulis* dwarf-herb community
CG13 = *Dryas octopetala-Carex flacca* heath
CG14 = *Dryas octopetala-Silene acaulis* ledge community
U1 = *Festuca ovina-Rumex acetosella* grassland
U2 = *Deschampsia flexuosa* grassland
U3 = *Agrostis curtisii* grassland
U4 = *Festuca ovina-Agrostis capillaris-Galium saxatile* grassland
U5 = *Nardus stricta-Galium saxatile* grassland
U6 = *Juncus squarrosusi-Festuca ovina* grassland
U7 = *Nardus stricta-Carex bigelowii* grass-heath
U8 = *Carex bigelowii-Polytrichum alpinum* sedge-heath
U9 = *Juncus trifidus-Racomitrium lanuginosum* rush-heath
U10 = *Carex bigelowii-Racomitrium lanuginosum* moss-heath
U11 = *Polytrichum sexangulare-Kiaeria starkei* snow-bed
U12 = *Salix herbacea-Racomitrium heterostichum* snow-bed
U13 = *Deschampsia cespitosa-Galium saxatile* grassland
U14 = *Alchemilla alpina-Sibbaldia procumbens* dwarf-herb community
U15 = *Saxifraga aizoides-Alchemilla glabra* banks
U16 = *Luzula sylvatica-Vaccinium myrtillus* tall-herb community
U17 = *Luzula sylvatica-Geum rivale* tall-herb community
U18 = *Cryptogramma crispa-Athyrium distentifolium* snow-bed
U19 = *Thelypteris limbosperma-Blechnum spicant* community
U20 = *Pteridium aquilinum-Galium saxatile* community
U21 = *Cryptogramma crispa-Deschampsia flexuosa* community

Chapter Four (Aquatic communities, swamps and tall-herb fens):
A1 = *Lemnetum gibbae* community
A2 = *Lemnetum minoris* community
A3 = *Spirodela polyrhiza-Hydrocharis morsus-ranae* community
A4 = *Hydrocharis morsus-ranae-Stratiotes aloides* community
A5 = *Ceratophylletum demersi* community
A6 = *Ceratophyllum submersum* community
A7 = *Nymphaeetum albae* community
A8 = *Nuphar lutea* community
A9 = *Potamogeton natans* community
A11 = *Potamogeton pectinatus-Myriophyllum spicatum* community
A12 = *Potamogeton pectinatus* community
A13 = *Potamogeton perfoliatus-Myriophyllum alterniflorum* community
A14 = *Myriophylletum alterniflori* community
A15 = *Elodea canadensis* community
A17 = *Ranunculus penicillatus* ssp. *pseudofluitans* community
A18 = *Ranunculus fluitans* community
A19 = *Ranunculus aquatilis* community
A20 = *Ranunculetum peltati* community
A21 = *Ranunculetumbaudotii* community
A22 = *Littorella uniflora-Lobelia dortmanna* community
A23 = *Isoetes lacustris/setacea* community
A24 = *Juncus bulbosus* community
A27 =
A28 =
S1 = *Carex elata* sedge-swamp
S2 = *Cladietum marisci* sedge-swamp
S3 = *Caricetum paniculatae* sedge-swamp

S4 = *Phragmitetum australis* swamp and reed-beds
S5 = *Glycerietum maximae* swamp
S6 = *Carex riparia* swamp
S7 = *Caricetum acutiformis* swamp
S8 = *Scirpetum lacustris* swamp
S9 = *Caricetum rostratae* swamp
S10 = *Equisetetum fluviatile* swamp
S11 = *Caricetum vesicariae* swamp
S12 = *Typha latifolia* swamp
S13 = *Typhetum angustifoliae* swamp
S14 = *Sparganietum erecti* swamp
S15 = *Acoretum calami* swamp
S16 = *Sagittaria sagittifolia* swamp
S17 = *Carex pseudocyperus* swamp
S18 = *Caricetum otrubae* swamp
S19 = *Eleocharis palustris* swamp
S20 = *Scirpetum tabernaemontani* swamp
S21 = *Scirpetum maritimi* swamp
S22 = *Glycerietum fluitantis* swamp
S23 = Other water-margin vegetation
S24 = *Peucedano-Phragmitetum australis* fen
S25 = *Phragmites australis-Eupatorium cannabinum* tall-herb fen
S26 = *Phragmites australis-Urtica dioica* tall-herb fen
S27 = *Potentillo-Caricetum rostratae* tall-herb fen
S28 = *Phalaridetum arundinaceae* tall-herb fen

Chapter Five (Maritime communities and vegetation of open habitats):
SM6 = *Spartina anglica* salt-marsh community
SM7 = *Arthrocnemum perenne* stands
SM8 = Annual *Salicornia* salt-marsh community
SM9 = *Suaedetum maritimae* salt-marsh community
SM10 = Transitional low-marsh vegetation with *Puccinellia maritima*, annual *Salicornia* species and *Suaeda maritima*
SM11 = *Asteretum tripolii* salt-marsh community
SM12 = Rayed *Aster tripolium* on salt-marshes
SM13 = *Puccinellietum maritimae* salt-marsh community
SM14 = *Halimionetum portulacoidis* salt-marsh
SM15 = *Juncus maritimus-Triglochin maritima* salt-marsh
SM16 = *Juncetum gerardi* salt-marsh
SM17 = *Artemisietum maritimae* salt-marsh
SM18 = *Juncus maritimus* salt-marsh
SM19 = *Blysmetum rufi* salt-marsh
SM20 = *Eleocharitetum uniglumis* salt-marsh
SM21 = *Suaeda vera-Limonium binervosum* salt-marsh
SM22 = *Limonio vulgaris-Frankenietum laevis* salt-marsh
SM23 = *Puccinellietum distantis* salt-marsh
SM24 = *Atriplici-Elymetum pycnanthi* salt-marsh
SM25 = *Elymo pycnanthi-Suaedetum verae* drift-line
SM26 = *Inula crithmoides* on salt-marshes
SM28 = *Elymetum repentis* salt-marsh
SD1 = *Rumex crispus-Glaucium flavum* shingle community
SD2 = *Honkenya peploides-Cakile maritima* strandline community
SD3 = *Matricaria maritima-Galium aparine* strandline community
SD4 = *Elymus farctus* ssp. *boreali-atlanticus* foredune community
SD5 = *Leymus arenarius* mobile dune community
SD6 = *Ammophila arenaria* mobile dune community
SD7 = *Ammophila arenaria-Festuca rubra* semi-fixed dune community
SD8 = *Festuca rubra-Galium verum* fixed dune grassland

SD9 = *Ammophila arenaria-Arrhenatherum elatius* dune grassland
SD10 = *Carex arenaria* dune community
SD11 = *Carex arenaria-Cornicularia aculeata* dune community
SD12 = *Carex arenaria-Festuca ovina-Agrostis capillaris* dune grassland
SD13 = *Sagina nodosa-Bryum pseudotriquetrum*dune slack community
SD14 = *Salix repens-Campylium stellatum* dune-slack community
SD15 = *Salix repens-Calliergon cuspidatum* dune-slack community
SD16 = *Salix repens-Holcus lanatus* dune-slck community
SD17 = *Potentilla anserina-Carex nigra* dune-slack community
SD18 = *Hippophae rhamnoides* dune scrub
SD19 = *Tortulo-Phleetum arenariae* dune annual community
MC1 = *Crithmo-Spergularietum rupicolae* maritime rock-crevice community
MC2 = *Armeria maritima-Ligusticum scoticum* maritime rock-crevice community
MC3 = *Rhodiola rosea-Armeria maritima* maritime cliff-ledge community
MC4 = *Brassica oleracea* maritime cliff-ledge community
MC5 = *Armeria maritima-Cerastium diffusum* ssp. *diffusum* maritime therophyte community
MC6 = *Atriplici-Betetum maritimae* sea-bird cliff community
MC8 = *Festuca rubra-Armeria maritima* maritime grassland
MC9 = *Festuca rubra-Holcus lanatus* maritime grassland
MC10 = *Festuca rubra-Plantago* ssp. maritime grassland
MC11 = *Festuca rubra-Daucus carota* spp. *gummifer* maritime grassland
MC12 = *Festuca rubra-Hyacinthoides non-scripta* maritime bluebell community
OV1 = *Viola arvensis-Aphanes microcarpa* community
OV2 = *Briza minor-Silene gallica* community
OV3 = *Papaveretum argemones* community
OV4 = *SperguloChrysamthemum segetum* community
OV5 = *Digitaria ischaemum-Erodium cicutarium* community
OV6 = *Cerastium glomeratum-Fumaria muralis* ssp. *boraei* community
OV7 = *Veronico-Lamietum hybridi* community
OV8 = *Alopecuro-Chamomilletum recutitae* community
OV9 = *Matricaria perforata-Stellaria media* community
OV10 = *Poa annua-Senecio vulgaris* community
OV11 = *Poa annua-Stachys arvensis* community
OV12 = *Poa annua-Myosotis arvensis* community
OV13 = *Stellaria media-Capsella bursa-pastoris* community
OV14 = *Urtica urens-Lamium amplexicaule* community
OV15 = *Kickxietum spuriae* community
OV16 = *Papaveri-Sileneetum noctiflori* community
OV17 = *Descurainio-Anchusetum arvensis* community
OV18 = *Polygonum aviculare-Chamomilla suaveolens* community
OV19 = *Poa annua-Matricaria perforata* community
OV20 = *Sagino-Bryetum argentii* community
OV21 = *Poa annua-Plantago major* community
OV22 = *Poa annua-Taraxacum officinale* community
OV23 = *Lolium perenne-Dactylis glomerata* community
OV24 = *Urtica dioica-Galium aparine* community
OV25 = *Urtica dioica-Cirsium arvense* community
OV26 = *Epilobium hirsutum* community
OV27 = *Epilobium angustifolium* community
OV28 = *Agrostio-Ranunculetum repentis* community
OV29 = *Ranunculo-Alopecuretum geniculati* community
OV30 = *PolygonoBidentetum tripartiti* community
OV31 = *Rorippa palustris-Filaginella uliginosa* community
OV32 = *Ranunculatum scelerati* community
OV33 = *Polygonum lapathifolium-Poa annua* community
OV34 = *Allium schoenoprasum-Plantago maritima* community
OV35 = *Lythrum portula-Ranunculus flammula* community

OV36 = *Lythrum hyssopifolia-Juncus bufonius* community
OV37 = *Minuartio-Thlaspietum alpestris* community
OV38 = *gymnocarpietum robertianae* community
OV39 = *Asplenietum trichomano-rutae-murariae* community
OV41 = *Parietarietum judaicae* community
OV42 = *Cymbalarietum muralis* community