Studies on the Degradation of Horn, Antler and Ivory at Archaeological Sites

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Horn, antler and ivory were in use extensively in the past. Prior to the synthesis of modern plastics these materials all had workable properties which made them extremely useful. The survival of these materials in the archaeological record is rare in comparison to the frequency of their use in the past, and this is made worse by the fact that they are also difficult to conserve. The literature suggests that study of these materials has been limited and that the methods of treating them after excavation are inadequate. A better understanding of the degradation of these materials within the environment and new methods of conservation treatment are needed. Furthermore, in order to identify the causes of degradation and the consequences for successful conservation, more research is needed into the nature and monitoring of the burial environment. Four different burial sites were selected for use in the study and their physical and chemical environments monitored and evaluated. Analogue samples of red deer antler, cattle horn and elephant ivory were buried at each site and retrieved after fixed time periods. Retrieved samples were analysed by weight loss, scanning electron microscopy (SEM) and microprobe analysis, Fourier Transform Infrared Spectroscopy (FTIR), X-ray diffraction (XRD), to establish amount of degradation which had taken place. Microbiological and biochemical evaluation suggested that collagenase production by microorganisms could play a role in the deterioration of ivory and antler within the burial environment. Analysis showed that horn samples were subject to substantial weight loss and FTIR indicated that protein breakdown had occurred. Environmental monitoring of the study sites gave a better understanding of the burial environment and the pace of deterioration. At the marine site, the slightly alkaline aerobic environment caused rapid degradation of protein by a combination of microbial attack and chemical hydrolysis, whereas the mineral component, hydroxyapatite, was protected by the seawater, leading to survival of antler and ivory but rapid degradation of horn. The brackish wetland proved to be the most protective for antler and ivory due to the waterlogged, reduced environment and presence of fine estuarine silt. Horn was usually found in extremely poor condition upon excavation, and required immediate conservation treatment since it is unsuitable for maintenance under passive conservation conditions. The estuarine environment has considerable potential for in situ preservation of organic materials, even horn, to a limited extent, and should be investigated further. Existing conservation treatments for antler and ivory are difficult, and only partially successful, so that if a suitable burial environment could be identified then preservation in situ could be an option. This study has shown that further development of new conservation treatments for these materials requires more information about the effect of the burial environment on the protein component. The development of models based on these data would also be useful in assessing how environmental change will impact on these types of artefacts at archaeological sites.
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ABBREVIATIONS

cm\(^{-1}\)  per centimetre
m  metres
mg/L  milligrams per litre
mV  millivolts
µS/cm  microsiemens per centimetre
BP  Bulk Precipitation
EDAX  Energy Dispersive X-ray Analysis
EDTA  Ethylenediaminetetraacetic acid
FTIR  Fourier Transform Infra-Red Spectroscopy
PBS  Phosphate Buffered Saline
XRD  X-ray Diffraction Spectrometry
RAMSAR  The Convention of Wetlands of International Importance
TDS  Total Dissolved Solids
TF  Throughfall
Tris  Tris(hydroxymethyl)aminomethane
SEM  Scanning Electron Microscope
SI  Saturation Index
WHO  World Health Organisation
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In memory of my sister Joy Dunford
AUTHOR’S DECLARATION

I hereby declare that the work presented in this thesis is my own and has not been presented previously or separately for any other award. All the work described herein was completed solely by myself with the exception of the chemical analysis of water samples which was conducted by The Royal Holloway Institute for Environmental Research. The physical analyses of soil samples were carried out by Forest Research and the Royal Holloway Institute for Environmental Research. The water samples at the freshwater wetland site at Fiskerton were collected and recorded by English Heritage, the interpretation of the data is my own.
CHAPTER 1

LITERATURE REVIEW

1. Introduction

The processes of deterioration are complex and encompass physical, chemical and biological mechanisms and combinations of all three. The rates and processes of deterioration are determined by the nature of the burial environment. Deterioration is inevitable since the burial environment is a dynamic complex system. By investigating the rates and processes of decay of archaeological materials in a variety of burial environments it may become possible to identify trends and processes causing decay to the buried materials and to measure the rates of deterioration in different burial environments. The environment is not fixed there are numerous mechanisms and processes which can cause it to change both natural and those caused by human activity. For example political decisions can instigate change within the environment. The current policy of managed retreat in coastal areas will cause environmental changes by allowing the influx of sea water into previously terrestrial or freshwater systems. Change is greatest at the interfaces between environmental zones such as the interface between:

- Terrestrial/Estuarine
- Terrestrial/coastal
- Estuarine (littoral)/submerged
- Coastal (littoral)/submerged.

It is important to understand how cultural resources are effected by environmental changes influenced by factors such as rising sea-level and coastal erosion. It would be interesting to be able to establish and quantify where the boundaries are between
dry/wet/waterlogged and submerged and between freshwater/brackish and saline and between aerobic and anaerobic conditions and to better understand the effects of these changes on buried archaeological materials. The archaeological resource can be separated into organic (e.g. wood, leather, bone, insects and pollen) and inorganic materials (e.g. stone and metal). It is generally accepted that materials which comprise high levels of organic composition are more susceptible to degradation than inorganic materials (Holden et al., 2006). However, in contrast, it should also be highlighted that the conditions which are favourable for organic preservation may not necessarily be unfavourable for the preservation of inorganic materials as well (Fell and Williams, 2004). Obviously the time period of burial is a critical factor in the degradation of an object as well as the amount of time it took for it to become buried. In the case of buried analogue samples the periods of burial were short in the context of archaeological time and so it would be likely that they would survive in these environments over these time scales.

The work presented in this thesis is concerned with research to establish the behaviour of ivory, antler and horn in different burial environments. Studies were aimed to determine how these materials changed over time and to identify the mechanisms that might be responsible for deterioration in archaeological environments. These materials were selected because they all have an organic component, and in the case of antler and ivory, include a mineral component, in a manner similar to bone, so that they are often classified together and treated similarly. These differences in composition may cause them to react differently in the burial environment, so whilst these structural differences may be subtle, they may potentially be significant and have implications for the way the materials are treated immediately post-exavcation and during conservation.
1.1. Characteristics of Archaeological Sites

Archaeological sites are not static; they evolve over time. There are two sets of biases found in the archaeological record; those created from the living context of the past and those of preservation. The condition of an object can be significantly affected either naturally or deliberately before it becomes part of the buried archaeological record. Objects may be broken accidentally or as part of a ritual, or they may become worn out before they are deposited (Hurcombe, 2007). The method of deposition can also affect their condition. Objects may be discarded or become lost leaving them exposed on the ground surface. In the past, objects have also been deliberately deposited, for example, antler picks in the ditches at Avebury or within the Neolithic flint mines at Grimes Graves (Clutton-Brock, 1984). There are also cultural factors to consider involving human interventions by activities such as ploughing or re-use of a particular site (Warscheid, 2008).

Objects may also be subject to environmental changes post burial, for example, inundation of land surfaces can change previously terrestrial burial conditions into wetlands or marine sites. For example, the North Sea inundation after the last ice age submerged many sites which are producing objects such as tusks (Turner-Walker, 1998). Sites within the inter-tidal zone are particularly vulnerable to changes in climate, including sea-level rise. Seahenge on the Norfolk coast was excavated in 1999 when it was decided that otherwise it would be destroyed by coastal erosion. Conversely, drying out of sites can cause dessication and erosion. The wetland site at Flag Fen has been threatened with dessication by drainage of the surrounding countryside to create farmland. There is an initial period of transformation where a particular site becomes buried. This involves natural processes such as:
(i) Mechanical, the effect of water, wind, erosion, silting and frost.

(ii) Chemical, acids and aerosols

(iii) Biological, animals and plant activity and growth, microorganisms.

The materials used in this study (horn, antler and ivory) are organic materials derived from cattle, deer and elephant, therefore they contain components which were alive and ultimately died.

In archaeology the death of an animal leads to:

(i) The manufacture of an object, or

(ii) The burial of the material.

Post-mortem processes occur in two broad environments:

(i) Biostratinomic processes, these are processes which occur between the death and final burial.

(ii) Diagenetic processes, these are the processes which take place following death and burial.

The science which unites the two disciplines is taphonomy, the study of all changes occurring in a substrate after death (Child, 1995). Bone, which has a similar composition to antler and ivory, deteriorates by three pathways after it becomes buried:

1. Chemical deterioration of the organic phase

2. Chemical deterioration of the mineral phase

3. Microbiological attack of the composite

The mechanisms of decay involve interactions between physical, chemical and biological processes (Collins et al., 2002).

By monitoring the environment it should be possible to assess the physical, chemical and microbiological changes which would be likely to occur in those particular
conditions. Three of the sites used in the study were environmentally monitored with chemical and physical conditions recorded. The parameters recorded were those commonly regarded as being significant in the preservation or deterioration of archaeological materials, (Gregory and Matthiesen, 2006). The environment provides the physical conditions, soil, precipitation, bedrock, groundwater regime, which create the chemical environment. The interaction of physical and chemical conditions determines the species of micro-organisms which can survive thereby creating the biological environment (Corfield, 2007). The interaction between the physical, chemical and biological conditions influences whether certain types of archaeological materials will survive or become degraded and determines the nature and extent of that degradation. Deterioration cannot be completely avoided but in some environments it occurs at a much slower rate (Gregory and Matthiesen, 2006). There is a reasonable amount of agreement regarding which elements within the burial environment, it is important to monitor, when assessing the potential for a site to be protective or degrading (Caple and Dungworth, 1998). Therefore it is possible to develop monitoring strategies which can be used to compare data between environments at different sites.

The broad outlines regarding the survival and degradation of the organic materials used in the study can be refined further by incorporating classifications of some of the most important factors concerning the deterioration or preservation of materials in the natural environment. Samples of red deer antler, cattle horn, and at two of the sites, elephant ivory, were buried and recovered at several time periods. It is also important to recognise that the way in which organic archaeological material becomes buried and then preserved or degraded is subject to large variations (Hurcombe, 2007). Within a stable environment conducive to its preservation, a material such as wood for example,
will deteriorate gradually turning into peat and then after millennia coal (McLeish, 1989). Post mortem taphonomic processes can cause changes to bone which can cause it to be preserved ultimately as a fossil. Dinosaur bone is a much altered substance from that present in a living animal but it still exists (Collins, 1995). Changes also take place post excavation when objects are removed from the burial environment and become part of the archaeological record. If they are not treated correctly and then maintained in the appropriate storage environments they will continue to decay (Watkinson, 1987). The same is true of objects on display in museums (Cassar, 1995). Soils, sediments and soil moisture content and water levels are important factors in determining the rate and type of degradation occurring in organic archaeological materials (Cronyn, 1990), as are chemical considerations such as pH, Eh potential, conductivity and concentrations of specific ions. Microbiological activity is also a factor in organic degradation and has a crucial role in catalysing a number of important reactions between sediment and water chemistry (Corfield, 2007).

The organic materials studied - horn, antler and ivory - are materials which were used extensively by man in antiquity (MacGregor, 1984). The preservation of archaeological sites and artefacts is favoured by low temperatures, natural dry conditions, artificial and natural preservation, i.e. salts, as well as low oxygen content of the surrounding environment (Warscheid, 2008). The environments described are those generally to be found in temperate climates. Dry arid environments can also preserve a wide range of materials but they are generally not encountered except in exceptional circumstances. Salt mines are an example (Harris, 2006).
Types of burial environment and their likely effect on archaeological materials are shown in Table 1.1. This table is adapted from (Watkinson, 1987) and illustrates the broad environmental conditions found within the burial environment, and their effects on specific archaeological materials. Interestingly horn is clearly picked out as a material but on closer inspection there is no mention of either antler or ivory. Bone however features regularly. Because of the similarity in composition of antler and ivory to bone they are often classified together and treated similarly. However there are differences in their composition and they react differently in the burial environment. Whilst these differences are subtle they are significant and have implications for the way the materials are treated immediately post excavation and during conservation. The general conditions present at each burial site were used to predict whether material was likely or unlikely to survive at each of the sites. The predictions relate to horn and to bone. Ivory and antler are not mentioned as they are generally treated in the same manner as for bone. The differences in their composition suggest that they have different requirements. In the table, environments are broadly categorised and the likelihood of the survival or the non-survival of the materials is noted.
Table 1.1 The effect of burial environments on archaeological artefacts (Watkinson, 1987)

<table>
<thead>
<tr>
<th>DAMP</th>
<th>Neutral</th>
<th>Acid</th>
<th>WATERLOGGED</th>
<th>Neutral</th>
<th>Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effect</td>
<td>slight Acid/Alkali</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Survival</td>
<td>Copper</td>
<td>Silver</td>
<td>Lead</td>
<td>Gold (and their alloys)</td>
<td>Porcelain</td>
</tr>
<tr>
<td>Possible</td>
<td>Copper</td>
<td>Silver</td>
<td>Lead</td>
<td>Gold (and their alloys)</td>
<td>Iron</td>
</tr>
<tr>
<td></td>
<td>Tin</td>
<td>Zinc</td>
<td>Glass</td>
<td>Shale</td>
<td>Wood</td>
</tr>
<tr>
<td>Unlikely</td>
<td>Copper</td>
<td>Tin</td>
<td>Lead</td>
<td>Zinc (and their alloys)</td>
<td>Iron</td>
</tr>
</tbody>
</table>

Gold | Slag | Porcelain | Shale | Wood | Leather | Textile | (silk, wool) | Keratin | Amber | Jet | Silver | (alloys) | Horn |
1.2. Preservation in Situ

It is important to be able to describe the relevant aspects of the burial environment to begin to understand the nature and importance of in situ preservation processes in waterlogged burial environments. However, there has been little previous research on the specific characteristics of waterlogged sites either in terms of the soil matrix and the composition of the ground water, or the interaction between the decay of organic archaeological materials and the burial environment (Caple and Dungworth, 1998). The need for long term in ground protection of the archaeological resource or in situ preservation is a stated objective of national and international agencies concerned with the future of the archaeological resource. If in situ preservation is to work then knowledge of the environment and its effect on archaeological materials is imperative and any data which adds knowledge regarding the effectiveness of these methods is useful (Van de Noort, et al., 2001). In situ preservation can only work if the threats to the archaeological resource can be understood and controlled (Corfield, 2007). There are a number of threats to the archaeological resource which can result in changes to burial contexts which may adversely affect organic archaeological remains buried within them.

There are a number of major environmental threats to the buried organic archaeological these include activities such as drainage schemes, which for example at the Iron Age site at Fiskerton in Lincolnshire was perceived to be damaging waterlogged organic archaeological remains by causing dessication when the site was converted into pasture land (Graham and Williams, 2008). Other threats include peat extraction (Van de Noort et al., 2001), aggregates extraction such as that at the Willingham gravel quarry in Cambridgeshire (French and Davis, 2004). Peat erosion, urban industrial expansion,
wetland habitat creation, water abstraction and conversion of pasture into arable lands also threaten the resource (Lillie, 2009). These changes to burial environments can lead to burial contexts fluctuating between dry and waterlogged as water tables rise and fall. Changing weather patterns are also a cause of threat to the buried organic archaeological resource. The stability of wetlands could be compromised by changes to the nature of inputs to catchment areas. Increased water inputs to the system have significant potential to cause changes in hydrology at the burial site and at catchment levels (Holden et al., 2006).

By monitoring the hydrology, physicochemical and biological status of burial environments it is possible to generate baseline data which will enhance understanding of the impacts of anthropogenic activities which may potentially damage the archaeological resource (French and Taylor, 1985). This baseline data also enables burial environments to be characterised (Cronyn, 2001). The major factors influencing preservation and degradation of organic archaeological materials which can and should be measured if possible include:

1. **Soil hydrology**, which relates to water table dynamics, including rising and falling water levels and hydraulic conductivity the movement of water through the soil profile. (Caple and Dungworth, 1998, Hogan et al., 2002).

2. **Soil chemistry**, which involves the measurement of redox potentials, oxygen, dissolved ions, pH and electrical conductivity (Caple and Dungworth, 1996).

3. **Microbiological assessment** of the soil profile. In addition to assessment of the microbiological activity of the soil profile it is also of interest to identify microbial deterioration within recovered organic archaeological material. This should lead to identification of specific microbes and fungi which are causing deterioration to particular materials within the environment.
A viable environmental monitoring strategy is essential in order to understand and characterise the waterlogged burial environment (Lillie and Ellis, 2007). Only after this has been successfully achieved will it be possible to recommend the most appropriate measurements with which to characterise different archaeological burial environments, and therefore preserve in situ organic archaeological remains.

1.3. Soils and waterlogged environments

1.3.1. Soils

Soil organic matter is derived from the breakdown of plant and animal matter. Soil water and its dissolved constituents is known as the soil solution and the soil atmosphere, the humid mixture of gases which fill the soil pores which are not filled by the soil solution (Rapp and Hill, 1998). The preserving potential of the buried environment is largely determined by the soil type and degree of waterlogging. Soils are composed of an organic and an inorganic fraction. The inorganic fraction is made up of sand, silts and clays which vary in particle size and in their ability to hold and retain water (French, 2003). Soils vary from sand to loams then through to fine grained silts clays with the development of peat in wetland environments providing additional types of burial environments. The composition of the soil determines the water balance and the hydraulic conductivity which ultimately influence the ability of the environment to preserve organic material (Corfield, 2007).

The sedimentary deposits are formed largely of secondary minerals, mainly the clay minerals (Fitzpatrick, 1986). Most water moves through the pores in soil and rock with the flow being controlled by the nature and distribution of the pore spaces. When the
pores are full the soil is saturated when they are not full the soil is unsaturated. The boundary between saturated and unsaturated soil is the water-table. Water in the saturated zone is ground water and water in the unsaturated zone is soil water. Within the vadose zone, which extends from the top of the ground surface to the water table, there may be saturated soils which are able to maintain preserving conditions depending on the capillarity of the soil. The maximum volume a particular soil can hold against gravity is its field capacity. The chemical interaction between a buried object and the soil is largely determined by the nature of the soil solution. Basic or calcareous soils provide better conditions for the preservation of molluscs, bone and carbonized materials. The principal factor influencing preservation within wet environments is thought to be the presence of saturation which reduces the levels of oxygen accessing sediments, thereby restricting the activities of aerobic bacteria (Lillie, 2007).

An environmental system which has achieved a near stable state where there is relatively little dynamism will affect any material introduced into it, initially at a higher rate but gradually more slowly as time progresses. The deposited material will itself achieve a relative equilibrium within the environment or it will continue to deteriorate until it is completely destroyed; the fate of the vast majority of archaeological material deposited by humans in the natural environment in the past (Hurcombe, 2007). After achieving a state where deterioration is slowed down by the nature of the environment the material will be relatively stable until the environment changes. If the equilibrium is disturbed any buried material will begin to decay again responding to the change in condition. Unless soils are waterlogged they are detrimental to the preservation of organic environmental evidence. Alternatively acidic soil conditions usually cause deterioration of bone remains but favour the preservation of plant and pollen material.
Once again only if water is present and air excluded will the survival of these materials be ensured.

1.3.2. Waterlogged environments

Wetlands as a word did not exist in the English Language prior to the 1960s. One of the earliest published uses of the term was in Scientific American in 1965. Therefore the term was coined in the United States of America principally as a growing concern regarding particular habitats (Van de Noort and O’Sullivan, 2006).

The Convention on Wetlands of International Importance, called the Ramsar Convention, is an intergovernmental treaty that provides the framework for national action and international cooperation for the conservation and wise use of wetlands and their resources. The Ramsar Convention is the only global environmental treaty that deals with a particular ecosystem. The treaty was adopted in the Iranian city of Ramsar in 1971. The Ramsar Convention takes a broad approach in determining the characteristics of wetlands. Under the text of the Convention (Article 1.1), wetlands are defined as "areas of marsh, fen, peatland or water, whether natural or artificial, permanent or temporary, with water that is static or flowing, fresh, brackish or salt, including areas of marine water the depth of which at low tide does not exceed six metres".

Five major wetland types are generally recognized under the convention:

- **marine** (coastal wetlands including coastal lagoons, rocky shores, and coral reefs);
- **estuarine** (including deltas, tidal marshes, and mangrove swamps);
- **lacustrine** (wetlands associated with lakes);
- **riverine** (wetlands along rivers and streams); and
- **palustrine** (meaning "marshy" - marshes, swamps and bogs).

In addition, there are human-made wetlands such as fish and shrimp ponds, farm ponds, irrigated agricultural land, salt pans, reservoirs, gravel pits, sewage farms and canals. Marine wetlands are considered to be wetlands up to a depth of six meters at low tide (the figure is thought to come from the maximum depth to which sea ducks can dive whilst feeding), but the treaty also provides for waters deeper than six meters, as well as islands, to be included within the boundaries of protected wetlands (Ramsar Convention Secretariat, 2006).

Wetlands are created as fresh-water flooding leads to the creation of bogs and fens by a process known as terrestrialisation. A depression collects water, gradually fills in and plant communities change according to the depth of water, nutrient availability and stability of the rooting zone (Charman and Warner, 2002). The results vary depending on the surrounding environment. In Highland areas terrestrialisation generally leads to the formation of sphagnum moss followed by peat formation resulting in raised bogs with a low pH. In lowland areas the same processes lead to the creation of nutrient rich peats and lowland fens. In both cases flooding creates waterlogged anoxic conditions and the accumulation of peat conditions conducive to the survival of organic archaeological objects (Hogan *et al*, 2006). Highland bogs tend to be acidic and favour the preservation of organic remains such as plants and pollen whilst lowland fens have a tendency to be alkaline and favour the preservation of organic remains such as molluscs and bone (French, 2003).
1.3.3. Estuarine environments

An estuary is a partially enclosed body of water formed where freshwater from rivers and streams flows into the oceans, mixing with the seawater. Estuaries and the lands surrounding them are places of transition from land to sea, and from fresh to salt water. Undisturbed sediments within estuaries and the coastal zone are often excellent preservers of waterlogged organic material (Hogan, et al., 2006). Natural processes, often modified in various ways by anthropogenic factors, are particularly dynamic within inter-tidal zones, where sustainability of sites can be questionable with both erosive (destructive) and depositional (protective) influences at work in a complex environment. Coastal erosion and rising sea levels lead to increasing environmental instability within the inter-tidal zone causing the exposure and degradation of large numbers of archaeological sites and their associated artefacts. Predictions of coastal change are further complicated by the uncertainties of global climate change. The part of the estuarine channel which is below mean low water is the subtidal zone.

The part of the channel situated between mean low water and mean high water is the intertidal zone. The upper intertidal zone and the supratidal zone above high water contain low energy waterlogged environments (Masselink and Hughes, 2003). The estuarine environment is characterized by having a constantly changing mixture of salt and freshwater, and by being dominated by fine sedimentary material carried into the estuary from the sea and from rivers. Estuarine sediments are formed from inter-tidal silts and mud, which can lead to the formation of salt marsh. These sediments are generally very fine and anoxic. These particular environments in the intertidal and supratidal zones with brackish flowing rivers are extremely promising environments in
regard to the *in situ* preservation of organic archaeological materials (Hogan *et al.*, 2006).

### 1.3.4. Marine environments

Seventy percent of the earth’s surface is covered by marine sediments (Konhauser, 2007). These sediments consist of three major components; inorganic detritus, organic matter and water and its solutes. The land derived (terrigenous), detrital content generally varies from coarse grained sands and silts to finer grained particles (clays). Marine sediments vary widely in composition and physical characteristics depending on water depth, distance from land variations in sediment source and the physical, chemical and biological characteristics of their environment. Marine sediments are subdivided on the basis of their depth of deposition:

- **Littoral**: 0 – 20 m
- **Neritic**: 20 – 200 m
- **Bathyal**: 200 – 2000 m.

There are also differences between deposits formed along the margins of continents and large islands which are affected by the proximity of land and occur mostly in shallow water and pelagic sediments which form in the deep oceans. Deposits in shallow coastal waters are sands. The controlling factors in marine sediment diagenesis are the solid-liquid exchange phenomena, pH, Eh and organic metabolic processes (Florian, 1987). Marine sediments are known to be good at preserving organic archaeological materials, if they are anaerobic deterioration can be slowed down considerably and material preserved. The numerous wooden shipwrecks located in marine sediments are proof of the preservation potential of the marine environment (Gregory, 2009).
1.4. The impact of water chemistry on preservation

The water chemistry, particularly the Eh potential, conductivity, dissolved oxygen levels pH and temperature, are significant factors relating to the preservation and deterioration of materials. Low levels of dissolved oxygen and a pH around neutral are generally considered to be the conditions favourable to the preservation of archaeological materials. Reduced environments are most conducive to the preservation of organic materials (Caple and Dungworth, 1998). Typical levels of specific ions encountered in groundwater are illustrated in Table 1.2 (Harter, 2003), compared with sea-water (Turekian, 1968) and with the permitted levels of these particular ions in drinking water (WHO, 1993). The table shows the levels of ions which would be expected to be found in particular circumstances, firstly in drinking water, secondly in normal groundwater systems and finally the levels generally found in sea-water.

Hydrolysis involves the reaction of water ions with ions of other solutes. It is measured by electrical conductivity and corresponds to the total solute content of aqueous environments (French, 2003). Conductivity is a measurement of the ease of passage of an electrical charge through a liquid and is the inverse of its resistance (Caple and Dungworth, 1998). Conductivity varies with the concentration and type of ions present within the solution. The level of conductivity is usually expressed in micro-siemens per centimetre (µS/cm) in normal fresh-water solutions or in siemens per centimetre in solutions with very high conductivity levels. Electrical conductivity provides an indication of the total ionic concentration in a system. Water with a high level of electrical conductivity is generally more chemically reactive than that with a low level of conductivity. Distilled water has a low concentration of ions and is therefore chemically unreactive whilst sea-water has an extremely high level of conductivity and
is highly chemically reactive with archaeological objects, particularly metals. In addition the electrical conductivity can be used to calculate the total amount of dissolved solids (TDS) in solution.

The Total Dissolved Solids (TDS), concentration in mg/L is approximately 65% of the electrical conductivity value in µS/cm. At a high TDS water becomes saline. Water with a TDS above 500 mg/L is not recommended for use as drinking water. Water with a TDS above 1,500-2,600 mg/L is considered problematic for irrigation (Harter, 2003). Sea water sites and estuaries contain high concentrations of ions due to the high levels of sodium chloride and therefore have high levels of conductivity. Environments which receive all of their water from rainfall tend to have low levels of conductivity generally around 100 µS/cm or less. Those environments which contain ground-water are generally higher than 100 µS/cm\(^{-1}\). Salt water environments are generally around 35,000 µS/cm\(^{-1}\) caused mainly by the high level of sodium chloride which is much greater in sea-water than fresh water. This data was compared with the concentration of these ions measured at the monitored sites. Measurements were recorded at all of the sites used in the study apart from the marine site which was not monitored.

The levels of pH and Eh potential drive the biological processes which degrade the materials under investigation. pH, redox reactions and hydrolysis are responsible for most processes that go on in the soil/water complex. Therefore they have an enormous effect on the preservation of organic remains within archaeological sites. Alkaline soil conditions favour the preservation of molluscs, bone and carbonized material. Without the addition of water to exclude air these soils usually degrade the majority of other organic material. Acidic soils usually destroy molluscs and bone but can allow the preservation of plant remains and pollen. The presence of water and the exclusion of air
are necessary to ensure the preservation of these types of organic remains (French, 2003).

Table 1.2 Major ion species present in water

<table>
<thead>
<tr>
<th>Ionic species</th>
<th>Concentration range (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Drinking water</td>
</tr>
<tr>
<td>Chloride</td>
<td>25</td>
</tr>
<tr>
<td>Iron</td>
<td>0.2</td>
</tr>
<tr>
<td>Sodium</td>
<td>200</td>
</tr>
<tr>
<td>Sulfate</td>
<td>250</td>
</tr>
</tbody>
</table>

1.4.1. Eh potential

Environmental conditions within the burial environment are commonly described as anaerobic or anoxic or as aerobic or oxic. Anaerobic conditions are oxygen excluding and reducing whilst aerobic or oxic environments are oxidising. Oxidation reactions involve the addition of oxygen and the loss of hydrogen during a chemical reaction and reduction involves the loss of oxygen and the gain of hydrogen (French, 2003). To maintain overall electrical neutrality the oxidation of one species in the system must be accompanied by the simultaneous reduction of another, this is known as redox. The concept of redox can be applied to the burial environment and measuring redox potential is the best way of measuring the presence of oxidising or reducing conditions. Oxidising environments are those in which there is a tendency for chemical species to lose their electrons, whilst reducing environments are those where chemical species take
up electrons from their surroundings. Within the environment this is expressed as the redox potential (Eh) and is measured in millivolts.

Eh potential gives an indication of the intensity of oxidation or reduction occurring in the soil system and can be measured at specific points (Gambrell and Patrick 1978). Soil micro-organisms oxidise organic materials during the process of respiration, using oxygen as an electron acceptor under aerobic conditions. When oxygen becomes depleted under anoxic conditions, ions such as $\text{NO}_3^-$, $\text{Mn}^{4+}$ and $\text{Fe}^{3+}$ becomes utilized in turn for electron transfer, the electron availability being measured by Eh potential. The categories of oxidation and reduction in terms of Eh potential are shown in Table 1.3. As the system becomes more reduced it becomes more protective of buried organic archaeological remains. This is due to the reduction in numbers of aerobic bacteria which cannot survive in highly reduced conditions (Hopkins, 1998).

Table 1.3 Eh potential categories of archaeological burial deposits (Cronyn, 1990)

<table>
<thead>
<tr>
<th>Eh potential category</th>
<th>Eh potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidising deposits</td>
<td>+700 to +400</td>
</tr>
<tr>
<td>Moderately reducing deposits</td>
<td>+400 to +100</td>
</tr>
<tr>
<td>Reducing deposits</td>
<td>+100 to -100</td>
</tr>
<tr>
<td>Highly reducing deposits</td>
<td>-100 to -300</td>
</tr>
</tbody>
</table>
1.4.2. pH

The measurement of pH gives an indication of the acidity or alkalinity of a solution and is measured on a logarithmic scale related to the hydrogen ion concentration (Pollard and Heron, 1996). The measurement of pH in soil solutions is achievable but can prove to be difficult for a number of reasons. The measurements can fluctuate markedly even over short distances and depths and over short periods of time. Fluctuations may be caused by microbial activity, by soil drying out or by seasonal variations in the amount of organic matter. The pH of soils and sediments can be a useful parameter in the identification of soil units and in understanding vegetation patterns. Archaeological material requires a neutral pH to remain stable. If the pH falls below 4 or rises to above 8, rapid deterioration may occur. As long as reducing conditions are maintained, pH is the major determinant in the survival or degradation of waterlogged archaeological remains.

Peat and mineral soils of the uplands together with raised bogs and sandy or gravely soils of the lowland are naturally acidic, whilst lowland fen peats, lake sediments, riverine silts and estuarine muds have much higher concentrations of dissolved salts and tend to be more neutral or alkaline. The pH range for soils is normally from pH 3 to 9. The classification of soil pH is shown in Table 1.4. Soil pH has been used to explain the degree of preservation of archaeological materials in different environments (Corfield, 2007). The acidity, neutrality or alkalinity of the burial environment will influence the preservation or degradation of differing archaeological materials in different ways. In waterlogged alkaline environments horn is unlikely to survive whilst in a waterlogged acidic environment its survival is possible (Watkinson, 1987).
Table 1.4 Classification of soil pH (Fitzpatrick, 1986).

<table>
<thead>
<tr>
<th>Classification of Soil pH</th>
<th>pH Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extremely Acid</td>
<td>&lt; 4.5</td>
</tr>
<tr>
<td>Very Strongly Acid</td>
<td>4.5-5.0</td>
</tr>
<tr>
<td>Strongly Acid</td>
<td>5.0-5.5</td>
</tr>
<tr>
<td>Moderately Acid</td>
<td>5.5-6.0</td>
</tr>
<tr>
<td>Slightly Acid</td>
<td>6.0-6.5</td>
</tr>
<tr>
<td>Neutral</td>
<td>6.5-7.3</td>
</tr>
<tr>
<td>Slightly Alkaline</td>
<td>7.3-7.8</td>
</tr>
<tr>
<td>Moderately Alkaline</td>
<td>7.8-8.5</td>
</tr>
<tr>
<td>Strongly Alkaline</td>
<td>8.5-9.0</td>
</tr>
<tr>
<td>Very Strongly Alkaline</td>
<td>&gt;9.0</td>
</tr>
</tbody>
</table>

Whilst pH is significant in relation to the degradation of organic materials it only gives
a part of the picture this is particularly true in wetland environments. Redox reactions,
hydrolysis and pH are together responsible for most of the processes which occur in the
burial environment. They have a tremendous effect on the preservation of organic
remains in soils including archaeological contexts (French, 2003).

1.4.3. pH/Eh Relationships

It has become common to plot Eh against pH in an attempt to characterise the natural
environment. Knowledge of both pH and Eh is extremely helpful in understanding the
likely chemical behaviour of that system (Pollard, 2006). There is a close relationship
between pH and Eh potential, which is particularly relevant in anaerobic waterlogged
Eh/pH diagrams have been used to illustrate monitoring results by plotting the
boundaries of water oxidation and reduction. This provides a clearer picture of the zones within which there is a likelihood of organic material being preserved (Corfield, 2006).

The measurement of Eh potential and the measurement of pH levels are two of the most important factors in the chemistry of waterlogged environments. By plotting the levels of Eh potential along the vertical axis of a diagram and pH along the horizontal axis it is possible to relate the chemical activity of the environment to boundaries within which waterlogged archaeological material should be stable. Eh potential can be said to reflect the abundance of electrons within the environment. A large number of electrons create a reducing environment while a low number create an oxidizing environment. pH represents the abundance of protons, large numbers of protons create acidity and low numbers create alkaline environments. As protons and electrons have opposite charges an abundance of one will cause a shortage of the other. Therefore oxidizing environments tend to be acidic and reducing environments tend to be alkaline (Brownlow, 1996).

At high Eh values water will be oxidised and at low levels it will be reduced. Similarly low levels of pH indicate an acidic environment and high levels an alkaline one. The most suitable levels for preservation of waterlogged archaeological materials are low Eh with a pH around neutral 7. As long as reducing conditions are maintained pH is a major determinant in the survival or degradation of waterlogged archaeological remains. pH values for waterlogged archaeological sites do not vary very much, with a pH range between 5-8 most commonly encountered. Waterlogged environments often exhibit signs of a reducing environment with depth, whilst the surface may show signs of more oxidising conditions (Caple and Dungworth, 1998).
The importance of the combined effects of pH and Eh on the survival of organic archaeological materials can be seen below in Fig.1.1.

Fig.1.1 The combined effects of pH and redox potential on the preservation of organic archaeological evidence (Campbell et al., 20011)

The diagram illustrates the conditions in which bone could be expected to survive.

Horn, antler and ivory are not highlighted in the diagram. Antler and ivory due to their
composition might be expected to survive in a similar environment to bone but as stated previously there are subtle differences in composition which make them behave in slightly different ways in response to the burial environment. Within an acidic burial environment the mineral component of antler and ivory will be dissolved whilst collagen dissolves in alkaline conditions. Horn decays rapidly in most burial environments and only rarely survives on archaeological excavations. If it survives at all it usually survives mineralised within the corrosion products of other deteriorated materials (Watkinson 1987).

1.4.4. Iron

Iron is most commonly present in soils in the form of Goethite which is hydrous iron oxide and a major iron ore. This is one of the commonest and most widespread of mineral deposits often forming iron pan capping oxidized sulfate deposits (Rapp and Hill, 1998). Iron may be precipitated if the Eh/pH balance becomes oxidised in higher Eh environments. This reaction is a good indicator of environmental status between moderately reduced and oxidised environments (Breuning-Madsen and Holst, 1998). Redox processes can lead to the concentration or removal of iron in certain soil horizons. Redox processes occur primarily in waterlogged soils where biological activity can cause the soil to become anaerobic reducing ferric iron. The more soluble ferric iron can then re-precipitate in other areas where oxygen is more plentiful. Iron species are reduced and generally mobile in low Eh environments. In free draining soil iron is usually present in the form of ferric hydroxides and ferric oxyhydroxides which give the soils a reddish colour. Some of the iron minerals responsible for these colours in freely drained soils are goethite [FeOOH], haematite [Fe₂O₃], lepidocrocite [FeOOH], ferrihydrite [Fe₃O₄] and limonite [FeOH(OH).ₙH₂O]. Waterlogged gleyed
soils tend to have iron present in its reduced state with minerals such as iron sulfide [FeS] and pyrite [FeS₂], which colour the soils grey/black or olive green.

These iron oxides can change in response to Eh variations for example if the environment becomes increasingly reduced soluble ion species become reduced from Fe³⁺ to Fe²⁺ and conversely if the environment becomes increasingly oxidised the soluble iron species are oxidised from Fe²⁺ to Fe³⁺. Where soluble iron is present within sediments ionic exchange occurs which can lead to the breakdown of collagen resulting in changes to the crystal structure of the mineral component of antler and ivory. This causes an increase in the porosity of the materials resulting in ion exchange and the subsequent deposition of the iron minerals. As a consequence waterlogged antler and ivory are often heavily stained by surrounding sediments. The presence of iron can disrupt disulfide bonds in proteins because of its high affinity and attraction for sulfur (Konhauser, 2007). Hydroxyapatite, the major mineral component of ivory and antler, is known to undergo alterations such as ionic exchange, cationic exchange and substitution of phosphate with carbonate. Under aerobic conditions iron acts as a catalyst to cause oxidation of sulphur dioxide which forms sulphuric acid. This sulphuric acid then causes solubilisation of collagen by hydrolysis (Florian, 1987).

In reduced conditions there are a number of organisms which use ferric iron as an electron acceptor. Many of these organisms also reduce nitrate and as they are facultative anaerobes they can also utilise oxygen. Organisms which are capable of catalyzing the reaction belong to Micrococcus, Bacillus, or Desulfovibrio. (Godfrey, 2007).
1.4.5. Oxygen

The presence of oxygen within terrestrial soils is principally due to the flow of oxygenated waters through the soil (Hopkins 1996). Free oxygen is dependent on the water balance which is the flow of water in and out of a system and hydraulic conductivity which determines the ease with which water can move through the fractures or pore spaces of the system. The rate at which oxygen is taken up by aerobic bacteria also influences the amount of oxygen present. However the water in marine and estuarine sediment is generally stagnant and in these sediments the renewal of oxygen becomes dependant on the relatively slow microscopic processes of molecular diffusion. Oxygen is an oxidising agent, therefore its presence in the burial environment is responsible for a number of redox reactions which can effect archaeological materials. The presence or absence of oxygen also controls the level and type of micro-organisms which in turn directly affect the decay or preservation of organic materials (Cronyn, 1990).

1.4.6. Sulfur

Sulfur is one of the commonest elements on earth and is commonly found within soils and sediments. In aerobic conditions it is present as sulfate and in anoxic conditions it is reduced to sulfide by sulfate reducing bacteria. The sand on many beaches is rich in organic matter, below the sandy surface the sand often turns black. In this region sulfate reducing bacteria react with sulfur present in the organic matter to produce hydrogen sulfide. This then reacts with iron present in the sand and in anaerobic conditions produces black iron sulphide. This may reduce the pH in areas such as estuaries (Masselink and Hughes, 2003), which in turn may be detrimental to the survival of minerals such as hydroxyapatite in antler and ivory (Heritage et al., 1999). The staining
of organic materials by these sediments, particularly those which are rich in reduced iron, is a particular problem (Godfrey et al., 2002). The presence of iron sulfides within archaeological materials such as fossil bone and waterlogged wood is a cause of great concern for conservators trying to stabilise these materials particularly as they become oxidised after excavation.

1.5. Influence of the biological environment on buried materials

Bacteria can be divided into aerobes that require oxygen for their metabolism and anaerobes that do not. Anaerobes are then divided into facultative and obligate anaerobes. Facultative anaerobes are responsible for depleting wetlands of oxygen, reducing the redox potential and creating the anaerobic environments that enable the preservation of organic wetland archaeological evidence (Corfield, 2007).

There are a number of genera of bacteria which are capable of reducing sulfate and extracting energy; *Desulfovibrio* and *Desulfotomaculum* are just two examples. These organisms utilize sulfate as a terminal electron acceptor in the oxidation of organic matter. Sulfate reducers are obligate anaerobes and are found only in anoxic sediment and anoxic water. Strongly reduced conditions are found beyond the region where sulfate is reduced to sulfide as this reaction is mediated by anaerobic bacterial activity. Highly reducing conditions where the pH is around neutral are good for the preservation of organic materials as the dormancy of aerobic bacteria slows the rate of degradation (Cronyn, 1990).

In marine sites, the largest populations of bacteria exist at the sea-water-sediment interface. In surface sediments rich in oxygen, aerobic bacteria dominate. Oxygen levels drop as aerobic oxidation of organic material occurs, facultative bacteria become
dominant and finally under anoxic conditions anaerobic bacteria dominate. Bacteria recycle organic material. On the depletion of oxygen anaerobic sulfate reducing bacteria continue to oxidise organic material (Canfield et al, 2005).

In a wetland, marine or estuarine environment aerobic bacteria will function until the available oxygen is depleted creating reducing conditions. In these reducing conditions, there will be anaerobic bacteria. If conditions change causing an influx of fresh oxygen, oxidising conditions will re-establish and the dormant aerobic bacteria will become active again (Corfield, 2007). The relationship between chemistry and microbiology in the environment is shown in Table 1.5.

**Table 1.5** The relationship between chemical and biological factors within the environment (modified from Corfield, 2007)

<table>
<thead>
<tr>
<th>Eh potential</th>
<th>Category</th>
<th>System</th>
<th>Class of microbes</th>
</tr>
</thead>
<tbody>
<tr>
<td>+500 to +350</td>
<td>Oxidised</td>
<td>Oxygen disappearance</td>
<td>Aerobes</td>
</tr>
<tr>
<td>+350 to +100</td>
<td>Slightly reduced</td>
<td>Nitrate disappearance</td>
<td>facultative anaerobes</td>
</tr>
<tr>
<td>below +400</td>
<td>Slightly reduced</td>
<td>Mn(^{2+}) formation</td>
<td>facultative anaerobes</td>
</tr>
<tr>
<td>below +400</td>
<td>Slightly reduced</td>
<td>Fe(^{2+}) formation</td>
<td>facultative anaerobes</td>
</tr>
<tr>
<td>0 to -150</td>
<td>Moderately reduced</td>
<td>Sulfide formation</td>
<td>Obligate anaerobes</td>
</tr>
<tr>
<td>below -150</td>
<td>Highly reduced</td>
<td>Hydrogen methane formation</td>
<td>Obligate anaerobes</td>
</tr>
</tbody>
</table>

When the environment becomes more reduced the species of micro-organisms changes. In aerobic conditions the number of collagen and keratinophilic fungi and bacteria increase making these environments degrading to organic archaeological materials. Keratinophilic fungi are responsible for degrading keratin within the burial environment. They include a number of the Ascomycota a division of the kingdom Fungi (Sharma and Rajak, 2003). Bacteria such as *Bacillus subtilis* are also known to
degrade keratin (Cai et al., 2008). *Actinomycetes* also degrade keratin. The *Actinomycetes* are gram-positive organisms that tend to grow slowly as branching filaments which resemble fungi. Fungi of the genus *Ascomycetes* are also known to promote dissolution of apatite in bone (Child, 1995). Under normal soil conditions collagen is decomposed rapidly by enzymes collectively known as collagenases. The mineral component of bone is similar to that of antler and ivory and is thought to protect the collagen molecules from bacterial decay which slows down the rate of deterioration (Trueman and Martill, 2002).

### 1.6. History and methods of manufacture of the study materials

The materials selected for use in the research were heavily utilised in antiquity (MacGregor, 1984) and are still in use today. Ivory, antler and horn are organic materials which were originally parts of living animals. All of the materials have properties which were long ago recognised by man as being useful and were recycled into making objects which were either, functional and useful or artistic, decorative or symbolic. Gradually humans learned how to make these materials into useful objects in various ways, some simple and some complex. The use of horn, antler and ivory by man for functional and decorative objects stretches across a diverse range of cultures and from Palaeolithic times to the present day. Before the invention of synthetic polymers these materials were extremely common and they are regularly found during archaeological excavations.
1.6.1. Ivory

Ivory is a term used to describe material derived from walrus, hippopotamus, sperm whale and narwhal as well as elephant and mammoth. It was used throughout the ancient world with examples including the Lewis Chessmen and a wide range of items of walrus items produced by Inuit people. This study concentrates on elephant ivory. Ivory working has always been a luxury craft (Lasko, 1987). The material is rare and has working properties that make it highly desirable. Ivory is commonly worked by carving using stone or metal tools. It was used in ancient Egypt, Phoenicia and Crete in the manufacture of decorative knife handles, toilet articles and statuettes. In furniture manufacture it was made into panels and screens and also into luxurious ivory beds. Ivory combs and inlaid boxes were manufactured in Syria 3,000 years ago, and similar objects are still made today (Minney, 1991). The trade in ivory was extensive throughout the Roman period. However after the fall of the Roman Empire in the fifth century, the trade declined rapidly in northern Europe. It revived in the medieval period (Greep, 1987). The introduction of legislation designed to protect the elephant in modern times has lead to the growth of a large black market and a huge increase in ivory smuggling.

1.6.2. Antler

Antler has also been in use since the Palaeolithic period (Pettitt, 2008). Its composite structure gives it great stress resisting qualities, which make it ideal for the creation of tools. Many of the great Neolithic monuments of Europe were constructed with the use of antler picks (Clutton-Brock, 1984). In northern Europe antler was used in the manufacture of arrowheads that have been excavated from a number of Scandinavian sites dating to the prehistoric period (Tilley, 1996). During the Roman period the material was used in sword and dagger grips and handles. The manufacture of knife
handles is another craft that continues down to the present day. The material was also
used in the production of gaming pieces. Its ready availability made it a common and
widely exploited material. Antler was also commonly carved but the process was often
made easier by soaking the material in water which softens it.

1.6.3. Horn

Objects made from horn are known from pre-Dynastic and Dynastic contexts in Egypt.
Its uses included combs, handles and numerous types of vessels (Schaverien, 2006).
Classical authors such as Pliny refer to horns being used as symbols of power and
authority as well as for drinking vessels and medical practices (Hardwick, 1981). A
number of drinking horns have been recognised on Dark Age and later sites. Because of
its composition horn survives only rarely within the burial environment. The metal
accoutrements are often the only pieces of the objects to survive. Horn is both spark
proof and waterproof, which led to cattle horn becoming widely adopted for the
manufacture of priming horns. They remained in common use until the invention of the
cartridge in the nineteenth century. Horn enjoyed a more widespread use, being made
into general containers for carrying materials as diverse as coins and axle grease. The
lightness and toughness of horn led to its use in the construction of defensive helmets,
particularly in the Dark Ages. Its flexibility also made it useful in the construction of
composite bows and arrow nocks. Horn is comparatively soft and fibrous, and by
soaking and boiling it becomes possible to split it into thin sheets. These sheets were
used in the manufacture of lanterns and windows (Schaverien, 2006).
1.7. Structure of the materials

Before the invention and synthesis of modern polymers these materials were in common use. However their survival within the archaeological record is patchy with horn in particular being rarely discovered on excavations particularly within temperate climates. This suggests that the conditions within the burial environment would need to contain specific environmental conditions to cause these materials to be preserved. Because the structures of the materials vary slightly in the case of ivory and antler and to a greater degree in horn, environmental conditions may not have the same effects on each of the materials. Therefore the environmental conditions would be hugely significant in determining whether a particular site would be protective or degrading to these materials. They would also determine whether the principle of preservation in situ, was a viable possibility for all, or some, or possibly none of the materials examined in this study.

1.7.1. Antler

Antlers are outgrowths of bone which are carried by most members of the deer family (Cervidae). Their principal function is to impress and they are important objects of display as well as combat. They grow annually from pedicles, small bony protuberances on the head of the deer which usually develop in the first year of its life. Antlers grow rapidly. This rapid growth causes internal canalisation of the internal antler structure, which in cross-section, gives the structure a sponge-like appearance with harder, denser bone material enclosing it. Because of the need to provide blood supply to the outer surface whilst the antler is growing and still covered in living tissue (velvet) the outer surface acquires a ridge-like appearance. This requirement for rapid growth affects the
structure of the material (Clutton-Brock and McIntyre, 1999). Whilst the antler is
growing it is provided with living tissue and a blood supply. At the same time it is also
slowly ossifying, with minerals being deposited from the tips downwards combining
with the protein collagen to provide a rigid bone-like structure which ultimately dies
and is then shed by the animal (Price and Allen, 2004). The ratio of mineral to organic
matter in antler is similar to that in bone. The collagen fibrils align to a common axis
giving bone its anisotropic qualities. Compact bone takes the form of lamellae which
are deposited concentrically around the longitudinal axis of the bone or antler and is
permeated by large and small channels. The whole system is connected by blood vessels
and on a fine scale both bone and antler are porous. Antler is a fast growing temporary
form of bone which has a plexiform structure permeated by blood vessels in the same
way as bone. In antler, these vessels are larger as a greater blood supply is necessary to
enable the antler to grow so rapidly. It is less mineralised than normal bone and has a
greater proportion of collagen. Antler is also 30% more flexible than bone and when
mechanically tested it has been found to be 2.7 times harder to break (MacGregor,
1984).

1.7.2. Ivory

Ivory is formed from teeth grown in the jaws of certain mammals, the best known and
in the case of this study, the most relevant, is the elephant. The major mineral
component is dentine which again has a similar composition to bone. It differs from
bone structurally in that the cells which mineralise the dentine are not incorporated
within the tissue as they are in bone but are lined up on the growing surface of the
dentine. This gives ivory a characteristic ring structure caused by dentine being
deposited in layers around the inside of the pulp cavity giving the ivory an acellular
prismatic structure (MacGregor, 1984). Dentine is formed from specialised cells called odontoblasts. In the initial stages of formation another group of cells arranged in a subodontoblast tissue layer secrete an organic matrix of predentine which consists mainly of collagen fibres. These same cells are then responsible for the initial calcification of this matrix. Subsequently, the odontoblasts take over this process and as the secretion of further matrix continues the odontoblasts withdraw leaving the characteristic dentinal tubules along which extend the principal cell processes. As development continues the odontoblasts become more closely packed and take on a columnar appearance. Mineral salts are deposited in the form of spheres (calcospherites) interspersed with non mineralised tissue (Beeley and Lunt, 1980). In elephant tusks the pulp cavity remains open at the root and growth continues throughout the life of the animal. Tusks can grow to over 3 m in length and weigh 85 kg or more (Kunz, 1916). As the animal ages production is limited to maintaining equilibrium as material is worn away at the tips (MacGregor, 1984).

The major organic component of both ivory and antler is collagen. These materials also contain an inorganic component which is lacking in horn. Horn is almost entirely made up of the protein keratin. Both collagen and keratin contain sulfur, although it is more abundant in keratin than collagen. The formation of bonds between sulfur atoms is particularly significant in keratin. The protein from which collagen is assembled is secreted by cells in the form of procollagen which is subjected to a variety of chemical changes catalyzed by enzymes which result in the formation of mature collagen. The functions of collagens are always to provide tough reinforcing filaments in connective tissues. There are almost 20 types of collagens with around 30 different genes coding for the constituent polypeptides of these particular types (Elliott and Elliott, 2003). The
structure is maintained by three types of chemical bonding. The shape is maintained by hydrogen bonds, the chains are held together by peptide bonds with additional charged groups which are not held together by peptide bonds forming ionic bonds. These fibrils are then made into bundles to form long fibres from which tissue is formed. Collagen can be subject to hydrolysis particularly if the pH is more than 6.5.

The amino acid hydroxyproline is unique to collagen and can therefore be used to identify it (Cronyn, 1990). Hydroxyproline and proline are important for the stability of collagen (Nelson and Cox 2005) since they allow the twisting of the helix to take place giving it increased stability (Brinckman et al., 2005). Hydroxyproline is found in few other proteins and therefore it can be used as a measure of the amount of collagen. Hydroxylation of proline in the polypeptide chain requires ascorbic acid (vitamin C), which keeps an essential Fe$^{2+}$ atom in the enzyme prolyl hydroxylase, in the reduced form (Elliott and Elliott, 2003).

1.7.3. Horn

Horns are carried by animals such as cattle, sheep and antelope, and consist of a non-deciduous cuticle made from the protein keratin. The surface consists of a structure of fine parallel lines which distinguish the appearance of horn from that of bone, antler and ivory (Schaverein, 2006). Unlike ivory and antler keratinous tissues are not derived from bony skeletal material. They are formed on the body surface and function as exoskeletal elements. Keratin is synthesised in the epidermis, where cells gradually migrate from the innermost (malphigian) layer into a cornifying layer in which 3 strata are distinguishable namely stratum granulosum, granules of keratohyalin (soft keratin), stratum lucidum, a clear translucent layer of densely packed cells and then the stratum
corneum, which contains many layers of fully keratinised dead cells. Keratin is laid down in the actual cells which become overloaded and eventually die. In soft tissues such as skin, dead cells are continuously sloughed off. In hard tissues like horn they are retained permanently and added to from the underlying generative zone (MacGregor, 1984). Keratin can exist both as an amorphous matrix and as a long fibrillar molecule. The amino acids are joined together forming polypeptide chains caused by a condensation reaction when a molecule of water is lost as an amino acid reacts with the carboxyl group of another. In addition to intra and intermolecular hydrogen bonds keratins have large amounts of the amino acid cysteine. Cysteine contains sulfur and sulfur enables keratin to form disulfide bonds or bridges which confer additional strength and rigidity by cross-linking. Keratin is a highly reactive chemical because of the large number of side chains on the amino acids.

1.8. Processes of Deterioration

The nature of a specific burial environment will determine which processes are responsible for causing deterioration or protection to any material contained within it. The length of time which an object is buried is also a factor in determining whether or not it survives. Similarly the length of time which an artefact is exposed prior to it becoming buried will also have an impact on its potential for survival. The analogue samples used in this study were of antler, horn and ivory. They were all buried and recovered after specific time periods from the different sites used in the study. The physical, chemical and biological characteristics of the burial environment and the period of interment largely determine the condition of recovered organic artefacts, with microbiological activity critical in the early stages of deterioration particularly regarding ivory and bone like materials such as antler (Tripati and Godfrey, 2007). Horn decays
rapidly in most burial environments and only rarely survives on archaeological excavations. If it survives at all it usually survives mineralised within the corrosion products of other deteriorated materials (Watkinson 1987). On the site of the Mary Rose hundreds of wooden long bows survived but only one horn nock from the bows survived.

1.8.1. Physical Deterioration

In the burial environment repeated wetting and drying of materials can cause swelling and shrinkage leading to splitting and warping of these particular organic materials. When water is lost from the material the objects can split and warp. In atmospheric conditions ivory can split when subject to fluctuations in the levels of relative humidity (Lafontaine and Wood, 1982). Waterlogged antler can often break or crack when dried even after being treated (Hiron et al, 2005). Similar effects are caused by cycles of freezing and thawing. Due to its physical structure ivory is susceptible to a characteristic cone in cone splitting when subject to fluctuations in the level of relative humidity (Lafontaine and Wood, 1982). In the longitudinal aspect this causes lengthwise splitting along the lamellae. Degraded antlers have a number of disadvantages which make them vulnerable to various kinds of deterioration. They are sensitive to moisture content, as they dry they contract which can cause them to split and crack. The structure is brittle with few open pores which makes it vulnerable to osmotic pressures on drying. Physical damage such as cracking and warping and splitting, caused by wetting and drying can cause serious physical damage to ivory (MacGregor, 1984). When water is lost from horn, objects can split and warp. Antler can also split and warp on drying if collagen has been hydrolysed during burial. Low levels of relative humidity affect horn. When water
is lost from the material the objects can split and warp. Complete horns split longitudinally from the base upwards and exfoliate (Cronyn, 1990).

Physical disruption to materials is caused mainly prior to an object becoming buried and then immediately after it has been excavated. Before an object becomes buried it is exposed to surface environmental conditions and then to abrasion as the site begins to form. After burial it begins to reach equilibrium with the surrounding environment. However when it is exposed again it becomes vulnerable to physical changes caused by drying or by physical changes related to the crystallization and expansion of soluble salts. Ivory is susceptible to splitting caused by the expansion of soluble salts when an excavated object is dried (Watkinson, 1987). Objects recovered from marine sites should be carefully desalinated prior to any further treatment being undertaken. If soluble salts are not removed the objects can disintegrate as salts expand inside them on drying (Robinson, 1981).

1.8.2. Chemical Deterioration

Alterations in the chemical structure of a material can be caused by a number of factors within the environment, both ambient and buried. Chemical reactions can be caused by levels of acidity or alkalinity or oxidation and reduction, reactions between atoms and ions can all cause destructive chemical changes within the burial environment. Ivory and antler consist of two components, which are preserved at opposing pH. In acidic environments inorganic hydroxyapatite dissolves leaving soft organic collagen that shrinks on drying and causes warping of antler. In alkaline deposits the organic collagen hydrolyses and is attacked by bacteria. These conditions greatly influence the survival and degradation of antler and ivory. Horn is composed purely of the protein keratin and is susceptible to decay by hydrolysis and to attack by bacteria and fungi. Fossilization
occurs when inorganic calcium salts from the deposits replace the organic fraction of skeletal material (Collins 1995). This process is extremely slow in relation to animal bone and would not be expected in the course of normal excavation (Chadefaux et al., 2008). Collagen is less susceptible to decomposition than other proteins though it can hydrolyse in alkaline conditions. In these circumstances collagen can degrade leading to the disintegration of the material. Dentine loses collagen rapidly within the burial environment and is susceptible to rapid decay (MacGregor, 1984).

Denaturation (loss of shape of a protein) can be caused by extreme changes in pH and by the presence of heavy metal ions or by raising the temperature (Florian, 1987).

In a museum environment these materials can be subjected to adverse chemical reactions if they come into intimate contact with acid or alkali materials or are subjected to excessive levels of airborne pollutants (Cassar, 1995). Soils with a pH of less than 5 will promote demineralisation, the rate of demineralisation being dependent on a number of factors including, the pH of the soil, the concentration of chelating agents and the degree of water percolation. Soils low in phosphorus exhibit greater rates of demineralisation. Soils which are neutral or alkaline are better preservers of the mineral. The breakdown of collagen leads to the formation of more soluble peptides and amino acids, which are leached away into the environment (Hedges, 2002).

Calcium hydroxyapatite, \( \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \) can be changed by dissolution and recrystallization and by hetero-ionic substitution for example substitution by \( (\text{Fe}^{2+}, \text{Ca}^{2+}) \) creating in the case of iron substitution, the mineral vivianite, \( (\text{Fe}_3(\text{PO}_4)_2.8\text{H}_2\text{O}) \) and in the case of calcium substitution brushite, \( (\text{CaHPO}_4) \) and calcite, \( (\text{CaCO}_3) \). Environments containing high levels of \( \text{CaCO}_3 \) can cause the break-up of organic materials containing hydroxyapatite, the substituted \( \text{CaCO}_3 \) occupies more space in the mineral matrix than
calcium phosphate (Child, 1995). In acidic environments inorganic hydroxyapatite
dissolves leaving soft organic collagen that shrinks on drying and causes warping
(Cronyn, 1990). High levels of CaCO$_3$ would be normal in marine environments such as
Alum Bay, one of the sites used in the study, as the shells of marine molluscs consist
mainly of calcium carbonate which becomes part of the ocean floor sediment when they
die (Raisewell, et al., 1980). Alum Bay is also located close to the Needles rocks which
are large chalk stacks on the western extremity of the Isle of Wight and provide an
additional source of CaCO$_3$.

1.8.3. Biological Processes

Biological processes include:

- Biodegradation, the biological process which allows micro-organisms to recycle
  material in order for it to be used again by other organisms.
- Biodeterioration, is the term used when the material subject to attack by
  microbes is useful to humans and where any changes would bring about a loss in
  the value or quality of a given object (Urzi and Krumbein, 1994).

Microbial impacts on archaeological sites include three major phases (Warscheid, 2008)
1. The initial decay of vulnerable organic materials occurs soon after or even
   before they become buried due to the limited maintenance and care of the site in
   the initial months and years.
2. Post- burial biodeterioration processes occurring after burial followed by
   uncontrolled exposure to the prevailing environmental conditions of centuries.
3. Post- excavation biodeterioration. Microbial damage functions are stimulated
   again by changes in redox conditions during the enhanced access of humidity,
oxygen and nutrients supporting the contamination, infection and infestation of the excavated archaeological material by air or water-borne microorganisms.

Microbiological activity is particularly significant in the case of organic materials. A fundamental difference between environments is the presence or absence of available oxygen. Within an aerobic situation the level of dissolved oxygen is present in sufficient to ensure that the respiration and metabolism of communities of micro-organisms specifically bacteria, is not limited. An anaerobic environment limits aerobic metabolism because of the low level of available oxygen. Anoxic and anaerobic environments may then encourage the growth of bacteria which are capable of utilising other compounds as terminal electron acceptors such as sulfate reducers (Watkins, 2009).

Within the burial environment, initially aerobic oxidation of organic material occurs then facultative bacteria become dominant and finally under anoxic conditions at a depth usually between 40-60 cm anaerobic bacteria dominate. Bacteria recycle organic material. As oxygen is depleted by bacteria organic material continues to be recycled by sulfate reducing bacteria. Horn is composed purely of the protein keratin and although keratin is a resistant protein it is susceptible to decay by hydrolysis and attack by bacteria and fungi (Sibley and Jakes 1984). Keratinolytic fungi can denature horn by the process of sulfitolysis. The fungus releases sulfide which causes the breakdown of disulfide bonds present in the keratin (Sharma and Rajak, 2003). Fungi thrive in humid conditions. Their spores germinate at temperatures between 10-35°C and a relative humidity over 70%. The spores after germination produce hair like filaments called hyphae. These hyphae are the growing stage of mould which penetrate the material and grow on the surface.
Enzymes are proteins which catalyze most of the chemical reactions which take place in the body. The chemical compound on which the enzyme exerts its catalytic activity is called a substrate. Proteolytic enzymes act on their natural substrates, proteins and peptides by hydrolyzing one or more peptide bonds. As temperature increases the rate of most chemical reactions increases approximately twofold for every 10°C. The rate of catalysis by enzymes is dependent on the enzyme/pH activity profiles which vary from one to another but generally the optimum is around a neutral pH (Elliott and Elliott, 2003). The materials used in the study contain significant amounts of protein, collagen in the case of antler and ivory and keratin in the case of horn. These materials are potentially vulnerable to deterioration by microorganisms which is catalysed by enzymes and depends on the environmental conditions existing within the burial environment.

Four sites were used in the study, each deliberately chosen because it was felt they would provide a variety of environmental conditions which would cause the sample materials to deteriorate at different rates and by differing processes. The sites used in the study were terrestrial (Alice Holt), freshwater wetland, (Fiskerton), brackish wetland (Firestone Copse) and salt water marine (Alum Bay). Three of the sites had their environments monitored. The only site used in the study which was not monitored was the marine site at Alum Bay.
1.9. Research Strategy

1.9.1. Project Rationale

This research project sets out to determine the composition of horn, antler and ivory and to investigate their deterioration within the natural burial environment. These materials were utilised extensively in antiquity particularly prior to the synthesis of modern synthetic polymers (MacGregor, 1984). These materials are also purely organic in the case of horn and composite in the cases of antler and ivory which both contain a protein component within a mineral structure. By studying these particular organic materials it was felt that the nature of protein degradation and the influence of a mineral component in the preservation of the materials might be better understood. The major focus of this research is to relate the rate and processes of degradation, physical, chemical and biological to the environments in which objects are buried. At present, these factors are only poorly understood (Godfrey et al., 2002).

Sometimes individual processes are responsible for specific types of deterioration; usually a combination of deterioration processes occurs simultaneously within an object and between an object and its surrounding environment. The various aspects are related to a number of different academic subjects and disciplines, particularly archaeology, earth sciences and microbiology. The study was designed to adopt a holistic and multi-disciplinary approach in order to better understand the nature of the materials and the nature of their survival or deterioration in the archaeological record. The study sought to understand why the survival rates of these materials are so varied in different types of burial environment.
The parameters monitored in the course of the study were ones which were deemed to be the most likely to significantly affect the buried analogue materials. There were slight variations in monitoring equipment and sampling regimes between sites so only comparable data was used in the analysis of site environments. The only type of environment in which it might be possible for all three analogue materials to survive in the medium to long term would be a waterlogged environment with a neutral pH. The study site most closely resembling these conditions was the brackish wetland at Firestone Copse. By analysing material degradation of buried analogue samples it was possible to establish whether this site caused less degradation to the sample materials than the other sites studied.

By studying the environments within which materials were buried and by using a wide range of analytical techniques to study the recovered sample material it was expected that information regarding the processes and rates of deterioration of the materials would be discovered. It was felt that this could lead to the development of models which could more accurately predict the condition of archaeological horn, antler and ivory within specific burial environments.

It was also anticipated that increased knowledge of the behaviour of the materials within the burial environment would inform as to whether in situ preservation was feasible for archaeological objects made from these materials. By examining different materials within different types of burial environment it should be possible to establish in which types of environment particular types of material are likely or unlikely to be preserved in situ. By monitoring, analysing and modelling data it should be possible to predict with a reasonable amount of confidence what the extent of degradation of a particular material within a specific environment will be. By predicting the processes and rate of
deterioration it would then be possible to determine which materials and types of conservation treatment would be most suitable for treating these objects when they are recovered from real archaeological excavations.

1.9.2. Research Objectives

The aims of this project were to determine whether specific burial environments were suitable or unsuitable for the in situ preservation of archaeological horn, antler and ivory. The literature suggested that the processes of degradation relating to these materials were poorly understood and that the methods of treating them after excavation were inadequate. There is a great deal of information regarding the deterioration of bone within burial environments but little regarding horn, antler and ivory. Antler and ivory are similar in composition to bone in that they have a mineral and an organic component which vary slightly in chemical composition to bone. Horn is purely organic and was used to investigate whether a purely organic material would be more vulnerable to degradation than composite materials.

The objectives were:

- To determine the processes of deterioration of ivory, antler and horn by burying samples at selected sites to allow them to decay, and by retrieving them and analysing them at specific time intervals;
- To monitor the environment of the burial sites to establish the levels of chemical and biological activity within each site;
• By subjecting the samples to various scientific analyses, establish whether variations in the condition of the recovered samples could be attributable to parameters that have been monitored and recorded within the environment;
• To ascertain if the rate of sample decay varies significantly between different types of burial environment;
• To increase understanding of the nature of the relationship between hydrolysis of proteins and demineralisation;
• By studying previous conservation treatments assess the effectiveness of materials currently in use and suggest new methods of treatment which could be investigated in the future.

1.9.3. Experimental Design

The research was conducted over a four year period. Samples were buried at four selected sites to allow the materials to decay. The retrieval intervals of sample material varied between sites. This occurred as two of the sites were under investigation by English Heritage (Fiskerton and Alice Holt). The site at Alum Bay was being surveyed by the Hampshire and Wight Trust for Maritime Archaeology, samples could only be retrieved when the site owners were themselves conducting investigations at the sites.

1.9.3.1. Burial Sites

The sites used in the study were specifically selected for a number of logistical reasons:

1. They provided a wide range of differing environmental conditions, Alum Bay is a fully submerged marine site, Firestone is an estuarine brackish waterlogged site, Fiskerton is a freshwater wetland site and Alice Holt a terrestrial site. It was anticipated that the variety of environmental conditions prevalent at these
differing sites would lead to differences in the type and degree of degradation occurring on the analogue samples.

2. The sites had already been set up for environmental monitoring with the exception of Alum Bay, (Fiskerton by English Heritage, Alice Holt by the Forestry Commission, and Firestone Copse by David Hogan. Accessibility, all of the sites were accessible at various time intervals due to other activities taking place.

1.9.3.2. Environmental Monitoring

Monitoring stations were established at each of the study sites, with the exception of Alum Bay where the equipment required for monitoring marine environments was unavailable. Equipment used at Fiskerton and Firestone Copse was manufactured to British Geological Society Standards and followed patterns generally used by the Royal Holloway Institute for Environmental Research. Equipment included piezometers and redox probes. The stations monitored water chemistry at fixed intervals. The major environmental factors monitored included, soil hydrology, which relates to water table dynamics, including rising and falling water levels and soil moisture content. Soil chemistry, which involves the measurement of redox potentials, oxygen, dissolved ions, pH and electrical conductivity. These parameters were also recorded at Alice Holt by the Forestry Commission with some additional parameters and slightly differing monitoring equipment. Microbiological assay, it is also important to identify microbial deterioration within recovered organic archaeological material.
1.9.3.3. Materials Analysis

It is important to know the composition and structure of materials prior to undertaking a study into degradation so that the processes of degradation can be recorded and interpreted. Ivory and antler contain both a mineral component and an organic component. The mineral component consists mainly but not entirely of hydroxyapatite whilst the organic fraction consists of the protein collagen. Horn is purely organic being composed of keratin.

It was anticipated that the analysis of samples both before and after burial within the monitored site environments would provide a greater understanding of the rates and processes of degradation. Analysis of unburied samples provided data regarding the decay of these materials within the atmospheric environment. The condition of the recovered samples was analysed and compared with samples which had not been buried. Deterioration was visually observed on some recovered samples and described using methods adapted from a previous study undertaken with antler and ivory samples recovered from the burial sites. Therefore it was possible to compare the deterioration of the samples within each of the burial sites and to identify a number of the causes of deterioration.

A number of studies have been undertaken into the nature of the various materials (O’Connor 1987). These studies generally utilise analytical techniques which examine the mineral fraction of the objects and utilise differing techniques to examine the degradation of the organic components. The suite of analytical tools used in this study included SEM and EDAX to examine recovered samples and highlight physical deterioration and the presence or absence of microorganisms. FTIR was used to examine the changing ratios of protein and protein and mineral within samples.
recovered after various periods of time. XRD was used to assess if there was any change in mineral composition within the recovered samples. This had slightly disappointing results, particularly with horn as it has no crystalline structure. Weight loss calculations are particularly useful in monitoring the general levels of deterioration taking place within recovered samples. Microbiological evaluation would assess the ability of the powdered antler and ivory samples to be degraded by a collagenase indicating whether or not microorganisms were capable of causing deterioration of protein within the samples.

1.9.3.4. Evaluation and Recommendations

By studying the environments within which materials were buried and by using a wide range of analytical techniques to study the recovered sample material it was expected that information regarding the processes and rates of deterioration of the materials would be discovered. It was felt that this could lead to the development of models which could more accurately predict the condition of archaeological horn, antler and ivory within specific burial environments. By predicting the processes and rate of deterioration it would then be possible to determine which materials and types of conservation treatment would be most suitable for treating these objects when they are recovered from real archaeological excavations. It was also anticipated that increased knowledge of the behaviour of the materials within the burial environment would inform as to whether in situ preservation was feasible as a method for archaeological objects made from these materials.
CHAPTER 2

SITE DESCRIPTIONS AND SAMPLING REGIMES

2.1. Choice of Sites

Four burial sites were selected for use in the study. These four particular sites were selected for a number of reasons. In practical terms all of the sites were accessible. The brackish wetland site at Firestone Copse had been used for a similar type of study in previous years and so a large environmental database already existed relating to the study site and its immediate surroundings, (Hogan et al., 2006). The terrestrial site at Alice Holt and the freshwater wetland site at Fiskerton were both the subject of recent reburial and environmental monitoring studies, by English Heritage at Fiskerton (Fell et al., 2005), and by English Heritage in collaboration with the Forestry Commission at the terrestrial site at Alice Holt (Graham et al., 2007). The marine site, Alum Bay, has been the subject of ongoing archaeological investigations for a number of years. The site is a protected wreck site and work can only be undertaken by the Licence holders, in this case the Hampshire and Wight Trust for Maritime Archaeology. The Trust agreed to place the groups of samples on the wreck site and to retrieve them at the specified times. The Alum Bay wreck site has not been environmentally monitored but was used in the study because it is obviously environmentally different from the others and the opportunity for access outweighed the disadvantages.

The general location of the sites used in the study can be seen in Fig. 2.1. Fiskerton is an important Iron Age site located close by the River Witham in Lincolnshire. An Iron Age
wooden causeway was excavated in part in 1981 (Field and Parker Pearson, 2003). The causeway has been under fairly intensive arable farming and drainage regime for a number of years. Recently changes have been implemented to allow the water table to rise naturally. The effect that this change would have on the archaeology was unknown, so environmental monitoring was undertaken to observe any changes. This then allowed the opportunity to monitor the effects on buried samples. The Iron Age wooden causeway at Fiskerton was previously under fairly intensive arable farming and drainage until recent changes to land management in 2004 allowed water tables to rise. The effects of raising water levels on the already desiccated soil, archaeological structures and artefacts were not known, but it was assumed that making a dry wetland wet again would be beneficial. However, it was still possible that the introduction of different water chemistry and oxygen regimes on site could have been detrimental. A monitoring programme was conceived to assess the impact of the changes.

The site at Firestone is on the estuarine section of the Blackbridge Brook bordered to the east by Firestone Copse. It comprises a brackish wetland in the Wootton Creek estuary on the north coast of the Isle of Wight. Natural river discharge and tidal flows are now regulated by a sluice downstream at Wootton Bridge. The sluice comprises two hinged flaps, located beneath the bridge, which allow sea-water into the mill pond as the tide rises. On a falling tide, the retained water is released mainly over a weir although the sluices also remain partially open. The valley at the study site is about 100m wide, where most of the floodplain carries rank ungrazed grassland of sea couch (*Elymus pycnanthus*). At this point, the Blackbridge Brook follows a straightened channel course and is joined by a smaller stream which has a narrow, more sinuous channel. The brackish wetland site at Firestone was selected for use in the reburial study as it had already been extensively monitored during the course of a previous English Heritage
funded project. During the course of previous studies it was noted that the environment was brackish with a pH mainly around neutral. The site also had a reducing environment. These conditions are thought to be favourable for the preservation of organic archaeological materials (Hogan et al. 2006).

The marine site at Alum Bay was selected as it provides a fully marine saline environment which differs in nature from the other study sites. Alum Bay is the site of a wreck currently being investigated by the Hampshire and Wight Trust for Maritime Archaeology, (HWTMA) which they allowed to be used in this study. Alum Bay is located on the north-west coast of the Isle of Wight and forms a bay whose western extremity ends in the Needles Rocks. The wreck was brought to the attention of the Isle of Wight County Archaeological Centre by Steve Robbins, a local dive school owner, in 1991. The wreckage lay in 7 m of water tucked amongst the reefs of Alum Bay in an area of fine sand. It appeared cohesive, with iron fastenings and numerous copper pins projecting from the seabed. Early in 1993, it was proposed that the HWTMA take a primary role in co-ordinating work on the site. A core team brought together Nautical Archaeological Society trained divers from the Isle of Wight and the RAF Odiham diving club to conduct an evaluation survey during the spring of that year. The survey recorded copper pins, two rows of irons knees or deck supports and two large hawse holes within an area of wooden structure over 20 m long and 4 m wide. The remains appeared to be that of the upper, port section of a wooden vessel lying with the external planking face down in the seabed, oriented north-west to south-east. The visible features elevated above the seafloor were the internal fixtures and fittings. The lines of knees and iron supports running down the length of the vessel signified the remains of decks while the hawse holes, through which the anchor chain and ropes passed, indicated the bow at the north east end. The structure lies relatively flat on the seabed with all the
timbers interpreted as frames, broken along the south-west extremities. This may be an area around or just above the turn of the bilge where this port section may have parted company from the lower hull. The fieldwork programme was resumed in the summer of 1998 as part of the first year of the Solent Maritime Archaeology Project (SolMAP), the aim was to survey and plan the whole site using planning frames. This work and that in subsequent seasons resulted in the production of a full site plan shown in Fig. 2.10. On completion of the survey, the identity of the wreck was still uncertain so areas were selected for excavation to help resolve this longstanding question. Removal of the sand revealed components of the hull of the ship which were measured and compared to the plan of a Leda Class frigate. The match was striking. These similarities and the weight of evidence from other finds which include broad arrows on copper pins and structural elements, lead the HIWTMA to conclude that the wreck was part of HMS Pomone, which sank on the Needles in 1811.

The Woodland Burial Study was a collaborative project between the research section of the Forestry Commission (Forest Research) and English Heritage, to devise methodologies to study and determine how land-use (particularly woodland) and soils affect the preservation of archaeological remains in situ. The project involved specialists from different disciplines (environmental scientists, archaeological conservators and conservation scientists). The project built on a solid foundation of previous research undertaken by Forest Research including long term environmental monitoring and mineral weathering studies and incorporated archaeological aspects to utilise this data and to develop methodologies for monitoring and potentially modelling the archaeological burial environment. The project involved the burial, recovery and analysis of a range of modern analogue materials at Alice Holt forest in Surrey, a Forest Research monitoring site.
Fig. 2.1 Location of the four sites used in the reburial experiments, Alice Holt, Fiskerton, Firestone and Alum Bay
2.2. Site Descriptions

2.2.1. Alice Holt

Forest Research is undertaking the long term monitoring of forest ecosystems as part of a European-wide network called the Level II Programme. The programme had been established under European Union legislation in 1994 in response to concerns regarding acid rain, air pollution, forest decline and soil acidification caused by afforestation. The main objective of the network is to assess changes within forest ecosystems and to establish the causes of these changes. Ten UK sites have been intensively monitored to detect changes in the environment and condition of forest ecosystems and to determine the impact of woodland cover and depositional inputs into the soil (Graham et al., 2007). The location of the burial site within the woodland is shown in Fig 2.2.

![Fig.2.2 Location of the Alice Holt burial site shown arrowed within the surrounding area](image_url)
2.2.2. Firestone Copse

The site at Firestone had been previously monitored for an English Heritage project conducted to assess the suitability of the site for the reburial of waterlogged archaeological wood (Hogan et al., 2006). The location of the burial site at the Firestone 2 monitoring station at Firestone Copse is shown in Fig.2.3

![Fig.2.3 Location of the Firestone Copse burial site shown arrowed within the Wootton Creek estuary](image)

2.2.3. Fiskerton

The Iron Age site discovered near Fiskerton lies 2.5 km east of the village close by the road to Short Ferry. The monitoring project comprised two elements, the assessment of the burial environment through ground water monitoring, and the burial of modern analogues to investigate material deterioration.

The main aims of the project were to:

- establish base-line data for groundwater levels and quality;
• measure changes in these data over time;
• assess the impact of re-watering on the preservation of archaeological materials.

These aims were achieved by measuring water levels, pH, Eh, and the chemical composition of the groundwater. Material deterioration was assessed by examining archaeological and newly buried samples. The purpose of the work was to gather sufficient data to provide guidance on the future management of the archaeological site of Fiskerton. One critical question was the extent to which raising the water level artificially would impact (either positively or negatively) on surviving archaeological remains. It was agreed that water levels would remain unaltered for a year in order that baseline readings could be collected. The location of the site at Fiskerton is illustrated in Fig 2.4

![Fig.2.4 Location of the monitoring site at Fiskerton shown as arrowed](image-url)
2.2.4 Alum Bay

The Alum Bay site was not environmentally monitored due to the lack of suitable equipment. The requirements of monitoring water chemistry on a marine site are logistically difficult and the equipment is relatively expensive. The technology is available in the form of sondes attached either to data loggers or to monitoring stations which are connected by telemetry to computers via a web-site. The location of the Alum Bay site is shown in Fig. 2.5.

![Figure 2.5](image-url) Location of Alum Bay at the western tip of the Isle of Wight shown arrowed
2.3. Sample Installation

Samples of horn, antler and ivory were buried at Firestone Copse and at Alum Bay. No ivory samples were buried at Fiskerton or at Alice Holt because these two sites formed part of a larger reburial study which was being conducted by English Heritage and the number of material types which could be buried was restricted.

The project was initiated early in 2003 with the installation of the water monitoring points. The modern analogue materials were buried in December 2003, ten months before the water levels were deliberately raised in October 2004. This was achieved by the installation of clay and stone bunds in the north–south aligned drainage ditches on either side of the field. Monitoring points were established at five locations in the vicinity of a wooden causeway. At Fiskerton a 2 m length of 2.5 cm diameter plastic drainpipe with random holes drilled in it was used to contain the samples. Samples of red deer antler and cattle horn were fastened in netlon mesh and separated from each other with plastic cable ties. They were then inserted into the pipe and tied with marine cord to the bottom of the pipe and then to a hole 50 cm above the base. The samples were fixed in the bottom 50 cm of the 2 m tube so that environmental changes could be observed at this depth. The samples were buried at cluster 1, targeted at the reedy/silt sediment layer below the water table. The depth of sample burial and the sediment types are illustrated below in Fig. 2.6. The location of the antler and horn samples within the cluster 1 monitoring station is illustrated in the schematic diagram Fig. 2.7.
**Fig. 2.6** Diagram showing sample location, depth and type of sediments at Fiskerton

**Fig. 2.7** Location of the horn and antler samples within the cluster 1 monitoring station
A similar method was used for the installation of samples at Firestone, however the depth of samples in the pipes was fixed at a depth between 50 cm and 100 cm. Separate sample columns were used for each recovery period to ensure the remaining buried samples were undisturbed. A small amount of gravel was first placed in the base of each hole, on which the piezometer element was allowed to stand. The top of the plastic tube was then cut to sufficient length to extend a short distance above the ground surface in order to facilitate locating and carrying out measurements. With the piezometer placed in the hole, gravel was poured in until it reached the top of the porous element, to improve permeability and assist the collection of water into the tube. Material from the excavation of the hole was then packed back above the gravel layer. A plug of bentonite (swelling clay) in the form of dry pellets was poured in until the top of the layer was at a depth equivalent to the top of the soil horizon containing the porous element. This was to ensure its hydrological isolation from overlying layers. The remainder of the hole was then repacked with the spoil up to the ground surface. Finally a plastic cap was fitted to the top of the tube to preclude entry of rainwater and debris.

A different methodology was adopted at Alice Holt where the sediment was not so fluid and would not have flowed into the tubes therefore the environment within the tubes would have been different from the surrounding burial environment. The burial methodology needed to ensure the samples were incorporated within known soil horizons and made intimate contact with the soil. It was necessary to ensure that there should be minimal disturbance to the burial environment being studied and no interference should occur either between the samples or between the samples and the monitoring devices.
The samples were buried according to a system devised by Forest Research for burying the study minerals at the Level II monitoring sites. A location was selected within the perimeter of the Alice Holt monitoring site. A trench measuring 1.3 m by 1.1 m was hand excavated by Forest Research staff on 13th June 2005 to a depth of 1.2 m. During excavation, each of the soil horizons were separated out and retained to ensure backfilling in the correct horizon order. The antler and horn samples were buried in Netlon bags and were installed by excavating a hole in the trench wall, pushing the net bag in and infilling the hole with soil. The burial site and surroundings are illustrated in Fig. 2.8 and the location samples within the trench are shown in Fig. 2.9.

Fig. 2.8 The burial site and surroundings within the Forest at Alice Holt
At Alum Bay the pipes containing the samples were only 50 cm long. The sediment at this site is shallow and therefore the pipes were buried horizontally in a shallow trench dug into the seabed and then backfilled over the samples. The samples at the three waterlogged sites were all placed in perforated tubes, which are relatively easy to install and remove. The sediments at the waterlogged sites were usually fine-grained and it was expected that they would fill the tubes through the perforated holes thereby rapidly recreating the external environment within the tube. The site plan of the wreck site at Alum Bay and the location of the buried samples are illustrated in Fig.2.10.
Fig. 2.10 Plan of the wreck timbers and location of samples in Alum Bay

2.4. Environmental Monitoring Instrumentation

Monitoring stations were established at each of the study sites, with the exception of Alum Bay where the equipment required for monitoring marine environments was unavailable. Equipment used at Fiskerton and Firestone Copse was manufactured to British Geological Society Standards and followed patterns generally used by the Royal Holloway Institute for Environmental Research. Equipment included piezometers and redox probes. The stations monitored water chemistry at fixed intervals. Eh potential, conductivity, dissolved oxygen, pH and temperature were also recorded. These parameters were also recorded at Alice Holt by the Forestry Commission with some additional parameters and slightly differing monitoring equipment. The instrumentation used at Firestone had a number of similarities with the other sites and a number of methods used at Firestone were also used later by English Heritage at Fiskerton. The site at Alice Holt used a number of differing monitoring instruments because this site
had been monitored for a number of years previously by Forest Research as part of a larger woodland project (Graham et al., 2008).

2.4.1. Alice Holt

Throughout the burial period various types of monitoring data were collected by Forest Research staff. Some of this data formed part of the ongoing monitoring regime undertaken by Forest Research whilst additional sample collection and measuring devices were installed specifically to accompany the burial environment study. The samples were buried in June 2005. This was followed by an unusually dry summer whilst rainfall during the later part of the study was higher than average. Environmental monitoring data was collected by Forest Research close to the Alice Holt burial site every two weeks. Tension lysimeters collected soil solutions from depths of 0.1 and 0.5 m for chemical analysis. The analysis included pH, conductivity, ionic composition, dissolved organic carbon (DOC), alkalinity and saturation indices. Further environmental parameters monitored included rainfall, deposition volume and chemistry.

2.4.1.1. Bulk Precipitation (BP)

The collectors are located outside of the forest and collect rainfall, condensation from fog, dew and other types of wet precipitation. Data was used for the whole duration of the burial experiment (collected fortnightly). The data was collected fortnightly. The total amount of water collected from dew and rainfall is collectively known as bulk precipitation (BP).
2.4.1.2. Throughfall (TF)

Throughfall (TF) refers to the precipitation which falls within the forest itself and is collected on the forest floor after it has dripped through the trees. Ten collectors were located within the burial area. Data was obtained by analysing a bulk sample taken from these collectors. Interestingly the results varied throughout the year reflecting the forest cycle (Crow, 2008). During the period from April to mid May high levels of phosphate and potassium were recorded due to an abundance of faecal matter from caterpillars feeding on the new leaves in the tree canopy. Periods towards the end of the year showed increased peaks in phosphate and potassium due to leaching from fallen autumn leaves.

Generally there are higher concentrations of ions and higher pH in the TF than in the BP. This is due to the biological production of ions in the canopy which is subsequently washed to the forest floor by precipitation. The lower ion content and pH make the BP a more aggressive solution than the TF for most soil minerals, indicating that tree cover provides a slightly less degrading chemical environment than the environment outside the woodland area (Crow, 2008).

2.4.1.3. Tension Lysimeters

Tension Lysimeters are designed to collect soil solution in situ for use in chemical analysis, (pH, conductivity, ionic composition, dissolved organic carbon, alkalinity and saturation indices). Two tension lysimeters were installed in the burial horizons. A plastic cup was inserted into the soil horizon, connected to a glass collection bottle via capillary tubing. A sample was collected by creating a vacuum in the glass bottle which
in turn creates a vacuum down the tubing causing water to be drawn onto the cup extracting the soil solution.

The soil moisture was monitored by three lysimeters at two locations at depths of 10 cm and 50 cm within the burial site. The annual mean values showed a rise in pH and a decrease in some ions such as potassium and sulfate. These readings came from lysimeters which had been installed by Forest Research as part of their general monitoring programme and had been providing data since 1996. As part of the reburial project, new lysimeters were installed horizontally into the three burial horizons within the trench. The new lysimeters required a long settling in period but eventually the data they produced showed ion concentrations which were comparable to those from the old lysimeters. Levels of nitrogen and potassium were higher in the trench than the surroundings but this could have been caused by the location of the trench which was close to a tree.

2.4.1.4 Piezometers

Six standpipe piezometers were installed in augered holes near to the burial site. Three were placed on either side of the trench at different depths to collect water from each soil horizon. The piezometers were similar to those used at Firestone and at Fiskerton, they were installed using similar methodology. The length of the tubes was cut to size to correspond to the depths of the soil horizons. The location and depth of piezometers within the monitoring station at the site is shown in Table 2.1.
Table 2.1 Alice Holt summary of the location and depths of piezometers.

<table>
<thead>
<tr>
<th>Horizon</th>
<th>Piezometer Number</th>
<th>Wall</th>
<th>Tube Depth (cm)</th>
<th>Tube height above ground</th>
<th>Depth below ground (cm)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>A</td>
<td>0.43</td>
<td>0.05</td>
<td>-0.38</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Lower 0.13 taped up</td>
</tr>
<tr>
<td>1</td>
<td>4</td>
<td>C</td>
<td>0.43</td>
<td>0.05</td>
<td>-0.38</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>A</td>
<td>0.54</td>
<td>0.035</td>
<td>-0.505</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>C</td>
<td>0.55</td>
<td>0.035</td>
<td>-0.515</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>A</td>
<td>1.08</td>
<td>0.05</td>
<td>-1.03</td>
<td></td>
</tr>
<tr>
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<td>6</td>
<td>C</td>
<td>1.06</td>
<td>0.05</td>
<td>-1.01</td>
<td></td>
</tr>
</tbody>
</table>

A schematic diagram illustrating the monitoring instrumentation and the location of samples at the Alice Holt monitoring station is shown in Fig 2.11.

Fig.2.11 Schematic diagram illustrating the monitoring station and burial location of samples at the Alice Holt burial site
2.4.2. Firestone Copse

Three monitoring stations were established in a short transect across the floodplain. Each monitoring station was instrumented to a standard design, incorporating two piezometers at different depths and, at FIRE 2 the monitoring station used in the study, a dipwell to 100 cm depth to measure water table fluctuations was also installed. Redox probes were set at a wider range of depths. The arrangement of equipment and their depths is illustrated in Fig. 2.12. The immediate surroundings of the site are shown in the photograph Fig. 2.13. The approach taken to monitoring the environment was based on the techniques used to design and establish monitoring stations in previous wetland research programmes (Maltby et al., 1996). Each station was set up in the same way to monitor fluctuations in water table depth below the ground surface and the associated redox potentials. The water regime was investigated using piezometers installed to at least two depths, based on the soil/sediment profile. Redox probes were installed at a range of depths, each in triplicate, to determine the oxidation-reduction balance in response to water table fluctuations and the duration of waterlogging.

Piezometers are generally used to measure water pressure. Standpipe piezometers are set vertically in auger holes and comprise a perforated PVC tube, sealed at the base and connected to a PVC riser pipe. The body of the piezometer has a series of inlet holes and a porous plastic filter which enables water to pass in but precludes the entry of sand- and silt-sized particles. Where sufficient depth of soil/sediment permitted, each station included two piezometers set to intercept water at around 50 cm and 100 cm depth. Each piezometer is hydrologically connected to water-bearing material within specified depths but isolated from material above. In contrast, a dipwell is an open well into which water may pass from any point throughout the depth of the hole.
The piezometers used in the study had purpose-built tips, (Casagrande porous plastic element length 320 mm/diameter 35 mm with average pore diameter 60 µm and permeability $3 \times 10^{-4}$ m$^{-1}$ s$^{-1}$), constructed of PVC with perforations over a 20 cm length. Each tip was attached by a screw connector to a length of PVC tubing, cut to the required length in the field. The piezometers were installed in 6 cm diameter holes, augered to the required depth using a Dutch auger. A small amount of gravel was first placed in the base of each hole, on which the piezometer element was allowed to stand. The top of the plastic tube was then cut to sufficient length to extend a short distance above the ground surface in order to facilitate locating and carrying out measurements. With the piezometer placed in the hole, gravel was poured in until it reached the top of the porous element, to improve permeability and assist the collection of water into the tube. Material from the excavation of the hole was then packed back above the gravel layer. A plug of bentonite (swelling clay) in the form of dry pellets was poured in until the top of the layer was at a depth equivalent to the top of the soil horizon containing the porous element. This was to ensure its hydrological isolation from overlying layers. The remainder of the hole was then repacked with the spoil up to the ground surface. Finally a plastic cap was fitted to the top of the tube to prevent the entry of rainwater and debris. Site visits were made at 2-weekly intervals to measure water levels and associated Eh potentials. The depth of the water table was determined by lowering a length of flexible plastic tubing into the piezometer pipe, and blowing until bubbles were heard. (Alternatively, it is possible to use a purpose-designed electronic measuring device which is lowered into the pipe until contact is made with the water table, which causes a bulb to light up or a buzzer to sound this type of instrument was used at Fiskerton). The tube was then removed and the length measured. The depth of the water
table below the ground surface was calculated by subtracting the length of pipe exposed above the ground from the total length of the tube.

Probes measuring Eh potential were made to a standard design at the Royal Holloway Institute for Environmental Research laboratories. Each comprised a tip of 0.5 mm gauge platinum fused to a copper terminal wire, with the connection waterproofed by means of a sheath of heat-shrink sleeving. The opposite end of the wire, to be left exposed above the ground surface, had a short length of copper core exposed by paring back the sheath with additional sleeving applied to prevent water penetrating the inside of the wiring sheath. Prior to installation in the field, probes were rinsed with dilute hydrochloric acid and then distilled water, and calibration checked in the laboratory using a pH 4.0 solution of quinhydrone, which gives a reading of +218mV. Probes giving other values were discarded. The calibration is necessary in the measurement of Eh potential to ensure that the results are those of real and not relative values. Probes were inserted by either pushing directly into the ground (for shallow depth), or by making a hole to the required depth using a metal rod or small diameter auger, and pushing the probe in until firm contact was established with soil material at the base of the hole. A short length of wire was left exposed above the ground surface to make the connection when measurements were made. Because of the variability found in natural systems, three replicate probes were installed at each depth to enable a mean value to be used for the interpretation of results. The nest of replicate probes for each depth at each station was protected at the surface by means of a perforated metal plate, secured to the ground surface by metal pins (tent pegs), and through which the wires were allowed to protrude. A length of electrical cable, cut to the required size, was used for this purpose. At the brackish wetland Eh probes were installed using three replicates at each of three
depths (5, 50 and 100 cm) in order to represent conditions occurring in the topsoil and to coincide with the depths of piezometer elements.

Eh potential was measured (at two-weekly intervals) by means of a portable battery-powered pH/mV multi-meter (Hanna HI 9025) and a calomel half-cell reference electrode. The cable connection between the meter and the calomel cell was modified so that it split into two, the original leading to the calomel cell, and with a crocodile clip attached to the end of the branch to enable it to be connected to each redox probe in turn. The half-cell was inserted into the ground surface, adding distilled water if conditions were found to be dry, to ensure a good contact. Meter readings can drift when the system is first connected up, but this usually quickly stabilises. Readings were taken when a steady value was recorded, but if drifting continued to take place, the value was recorded after one minute, with a note taken of the direction of continued drift. After each reading was made, the crocodile clip was removed from the redox probe and reconnected to the next probe to be read.

Key:

P = Piezometer to 50 cm and 100 cm depth

D = Dipwell to 100 cm depth (only at station FIRE 2)

**Fig.2.12** The arrangement and depth of piezometers and redox probes at the Firestone Copse reburial site
2.4.3. Fiskerton

Each monitoring station consisted of clusters of piezometers (dipwells). At each location monthly measurements were made of water levels, pH, Eh, temperature and conductivity. The chemical constituent of the water was measured from one piezometer from cluster 2 (Graham and Williams, 2008).

The antler and horn samples were buried at a depth of 1.7m in the cluster 1 monitoring station. This was a depth which was below the water table before the rewatering began. Data acquisition was a two day process; water levels were recorded on day one with an audible dip metre, and then the boreholes were bailed out. On day two, samples of water were taken and redox, pH, conductivity and temperature measurements were recorded, by inserting individual probes into the sampled water. Data were originally read from a portable multimeter.

The piezometers were of similar construction to those used at both the Firestone site and at the terrestrial site Alice Holt. The method of installation of the piezometers was similar to that used at the monitoring stations at the Firestone monitoring site. Water levels were measured using an electronic dip-meter with audible depth indication. Additional data was recorded from water samples recovered in the field using samples
drawn from the piezometers with a bailer. Water chemistry was measured with a Pro-
Sys portable multi-meter analysing pH/mV, total dissolved solids, conductivity and
temperature, with individual probes for each parameter. To ensure that the piezometers
accurately reflected the ground conditions they were emptied two days prior to sampling
to allow them to refill with fresh water.

Further water analysis including measuring levels of lead, ammonia, nitrate, sulfide,
chloride ion, orthophosphate, silicate, sulfate, calcium, tin, manganese, iron and copper
were undertaken by the Environment Agency. Data acquisition took place over two
days every two weeks. Water levels were recorded on day one with an audible dip
metre, and then the boreholes were bailed out. On day two, water samples were taken
and Eh, pH, conductivity and temperature measurements were recorded by inserting
individual probes into the sampled water. Data was read from a portable multimeter.
Since it was possible that the process of purging and refilling, as well as bailing and
sampling were affecting the Eh results, creating opportunities for additional oxidation to
occur, in situ Eh probes were also installed. These additional probes were installed with
the assistance of David Hogan in May 2006. Additionally, one water sample was taken
from borehole 2b and sent to the Environment Agency for analysis for a range of
determinants (sulfate, calcium, chloride, ortho-phosphate, sulfide, silicate, iron,
manganese, copper, nitrite, nitrogen). The location of piezometers and boreholes in
relation to the monitoring stations is shown below in Fig. 2.14.
Samples of horn, antler and ivory were buried at Firestone Copse and at Alum Bay. No ivory samples were buried at Fiskerton or at Alice Holt because these two sites formed part of a larger reburial study which was being conducted by English Heritage and the number of material types which could be buried was restricted. The retrieval intervals between sites also varied slightly; again this was caused by accessibility issues. For example samples could only be retrieved from Alum Bay when the site was being surveyed by the Hampshire and Wight Trust for Maritime Archaeology and divers were available. The sites at Alice Holt and Fiskerton were being utilised by English Heritage to look at the degradation of metal objects at these particular locations. The antler and horn samples were buried and retrieved at intervals which coincided with the timetable.
of sample retrieval devised by English Heritage. The sample retrieval intervals used at each of the burial sites is shown in Table 2.2

**Table 2.2 Sample retrieval intervals from each of the burial sites used in the study**

<table>
<thead>
<tr>
<th>Site</th>
<th>Sampling interval (months)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3</td>
</tr>
<tr>
<td>Alum Bay</td>
<td>Horn</td>
</tr>
<tr>
<td></td>
<td>Antler</td>
</tr>
<tr>
<td></td>
<td>Ivory</td>
</tr>
<tr>
<td>Firestone Copse</td>
<td>Horn</td>
</tr>
<tr>
<td></td>
<td>Antler</td>
</tr>
<tr>
<td></td>
<td>Ivory</td>
</tr>
<tr>
<td>Alice Holt</td>
<td>Horn</td>
</tr>
<tr>
<td></td>
<td>Antler</td>
</tr>
<tr>
<td>Fiskerton</td>
<td>Horn Antler</td>
</tr>
</tbody>
</table>
CHAPTER 3
ENVIRONMENTAL INVESTIGATIONS OF THE SITES

3. Introduction

The burial environment at three out of the four sites used in the reburial studies was monitored. The marine site at Alum Bay was not monitored as the site is at an early phase of survey and investigation and the necessary equipment was unavailable. The site at Firestone Copse was monitored during the course of a previous reburial project and the monitoring data used is not contemporary with the burial and recovery of the samples. Therefore direct links between samples and specific environmental conditions at the site cannot be made. However the environmental monitoring data does provide a background picture of the environmental conditions at this particular site. The sites at Fiskerton and Alice Holt, were monitored during the period when samples were buried and recovered therefore this data is contemporary with the study period.

3.1. The Physical Environment

The depth and description of sediments at the burial sites are summarised in Table 3.1. The physical environment prevalent at the reburial sites is summarised in Table 3.2 which describes the type of sediment, moisture content and mean water levels at the monitored burial sites.
Table 3.1 Depth and descriptions of soils and sediments at the environmentally monitored sites

<table>
<thead>
<tr>
<th>Site</th>
<th>Depth cm</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alice Holt</td>
<td>37-74</td>
<td>Greenish grey (10Y 6/1) with common to many clear distinct fine reddish yellow (7.5YR 6/8) mottles, stoneless clay, moist; moderately coarse to strong coarse angular blocky structure; high packing density; very slightly porous Cretaceous clay (gault)</td>
</tr>
<tr>
<td></td>
<td>74-100</td>
<td></td>
</tr>
<tr>
<td>Firestone</td>
<td>100-135</td>
<td>Light brownish grey (10YR 6/2) silty clay with many medium and coarse (peaty?) areas of black (N 2/-)</td>
</tr>
<tr>
<td>Fiskerton</td>
<td>100-170</td>
<td>Reedy silts</td>
</tr>
</tbody>
</table>

Table 3.2 Physical environment at the reburial sites used in the study

<table>
<thead>
<tr>
<th>Site</th>
<th>Physical Environment at the burial sites</th>
<th>Sediment</th>
<th>Classification</th>
<th>Mean water level (cm)</th>
<th>Mean soil moisture content%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alice Holt</td>
<td></td>
<td>stoneless</td>
<td>damp</td>
<td>-75</td>
<td>97.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>silty clay</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fiskerton</td>
<td></td>
<td>reedy silt</td>
<td>freshwater/waterlogged</td>
<td>-110</td>
<td>-</td>
</tr>
<tr>
<td>Firestone</td>
<td></td>
<td>estuarine silt</td>
<td>brackish waterlogged</td>
<td>-76</td>
<td>53</td>
</tr>
<tr>
<td>Alum Bay</td>
<td></td>
<td>sandy/silt</td>
<td>marine waterlogged</td>
<td>submerged</td>
<td>-</td>
</tr>
</tbody>
</table>

- No data

The sediments at Alum Bay have not been scientifically described and so have not been included in the descriptions in Table 3.1. By visual observation, they have been described as consisting of sand above a layer of sandy silt, they are so shallow that the
50 cm long tubes containing the samples could not be inserted vertically into them before hitting the bedrock and so they were laid horizontally within a shallow trench within the upper layer of sediment.

### 3.1.1. Soils/sediments

At Fiskerton the soil sequence at the monitoring site consisted of shell rich organic silts immediately below the plough soil. Beneath this layer is either degraded woody peat or fibrous peat with sandy lenses. Below these layers there is reedy silt, sandy palaeosol, or grey clayey silts. The depth at which the samples were buried (1.7 m), was below the water table so the soil at this depth (reedy silt) remained saturated throughout the study period. The sediment profile at the Fiskerton environmental monitoring stations is shown in Table 3.3.

**Table 3.3** Soil descriptions at the Fiskerton Cluster 1 and Cluster 2 burial sites

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Depth (m)</th>
<th>Soil description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0-0.2</td>
<td>Topsoil/ploughsoil</td>
</tr>
<tr>
<td></td>
<td>0.2-0.8</td>
<td>Shelly silts</td>
</tr>
<tr>
<td></td>
<td>0.8-1.20</td>
<td>Degraded peat</td>
</tr>
<tr>
<td></td>
<td>1.20</td>
<td>Top of reedy silts</td>
</tr>
<tr>
<td>2</td>
<td>0-0.25</td>
<td>Ploughsoil</td>
</tr>
<tr>
<td></td>
<td>0.25-0.52</td>
<td>Shelly silts</td>
</tr>
<tr>
<td></td>
<td>0.52-0.80</td>
<td>Degraded woody peat with wood</td>
</tr>
<tr>
<td></td>
<td>0.80-1.50</td>
<td>Reasonably well preserved peat</td>
</tr>
<tr>
<td></td>
<td>1.50-2.00</td>
<td>Reedy silt</td>
</tr>
</tbody>
</table>
At Alice Holt the soil is a mineral soil derived from the bedrock beneath. Unlike the other sites the soil is not saturated. The soil varies only slightly throughout the profile from stoneless silty clay to stoneless clay at the base of the horizons. During the burial period soil samples were collected for chemical analysis from each of the different soil horizons. Ten grammes of sampled soil was mixed with distilled water then shaken on an orbital shaker for 24 hours. The solutions were then centrifuged, filtered and analysed.

The surface 3cm of soil comprised the leaf litter which falls from the deciduous canopy of the woodland in autumn and is therefore highly organic made up mainly of oak and ash leaves. The soil is a surface water gley (Pelo-stagnogley), seasonally waterlogged and poorly drained. The boundaries between some of the soil horizons were indistinguishable and therefore they were combined for the purposes of this study (Ah combined with E; Btg combined with BCg). The soil descriptions from the Alice Holt burial site are shown below in Table 3.4.
Table 3.4 Soil horizon descriptions at the Alice Holt environmental monitoring station

<table>
<thead>
<tr>
<th>Burial Horizon number</th>
<th>Depth Sample</th>
<th>Depth (m)</th>
<th>Soil Type</th>
<th>Brief Soil Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0 – 0.07</td>
<td>Ah</td>
<td>Brownish black (10YR 3/2) stoneless silty clay. moist; moderate fine to granular subangular blocky structure with ped face colours as matrix; low packing density; moderately porous; moderately weak ped strength; slightly sticky and plastic; common very fine to coarse roots; common earthworm activity; non-calcareous; diffuse wavy boundary</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.15-0.37</td>
<td>E (g)</td>
<td>Greyish yellow brown (10YR 6/2) with many very fine bright yellowish brown (10YR 6/8) mottled stoneless silty clay. moist; moderately coarse subangular blocky structure; moderately weak soil and ped strength; slightly sticky and plastic; non calcareous; diffuse wavy boundary.</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.9</td>
<td>C (g)</td>
<td>Cretaceous clay (gault)</td>
<td></td>
</tr>
</tbody>
</table>

At Firestone the site consists of permanently waterlogged estuarine silt with brackish water and varying levels of salinity (Hogan et al., 2006). Water flow is controlled by sluices but the environment is influenced by the sea; it is much more saline than the site at Fiskerton, though not as saline as the fully marine site at Alum Bay. Details of the stratigraphy of the deposits at the brackish wetland burial site indicated mineral deposits of predominantly silt and clay to a depth of over 5 m overlying basal Oligocene clays.

The soils are predominantly clayey groundwater gleys developed in estuarine alluvium. Profiles are silty clay or clay throughout, with upper layers greyish with rusty mottles.
which are generally associated with oxidation and may be indicative of fluctuations in the water table, probably due to summer seasonal draw-down. Lower layers are generally unmottled and frequently bluish grey, indicating intense gleying associated with permanently saturated anaerobic conditions. A loose bag sample was taken of each major soil horizon and analyses were carried out to aid characterisation of the soil and confirm/supplement field observations. Laboratory determinations on soil samples were as follows: particle-size class (texture), easily oxidisable carbon, pH, moisture, total phosphate, potassium, sodium, calcium, magnesium, manganese, iron, chloride and sulfate (Hogan et al., 2006). Soils were described from purpose-dug pits at the location of each monitoring station, to about 50 cm depth (more or less coinciding with the position of the water table), with material below described from auger borings down to a maximum of 1.2 m depth. Descriptions are based on characteristics described in the Soil Survey Field Handbook (Hodgson, 1981) with colours identified from Munsell Soil Color Charts. The descriptions of the sediments at Firestone are shown in Table 3.5.


Table 3.5 Soil descriptions at the Firestone environmental monitoring station

<table>
<thead>
<tr>
<th>Station code</th>
<th>FIRE 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location</td>
<td>Mid-point of floodplain</td>
</tr>
<tr>
<td>Parent material</td>
<td>Estuarine alluvium</td>
</tr>
<tr>
<td><strong>Depth (cm)</strong></td>
<td><strong>Description</strong></td>
</tr>
<tr>
<td>100-135</td>
<td>Light brownish grey (10YR 6/2) silty clay with many medium and coarse (peaty?) areas of black (N 2/-)</td>
</tr>
<tr>
<td>135-175</td>
<td>Very dark grey (10YR 3/1) silty clay with common medium and coarse dark areas as above</td>
</tr>
<tr>
<td>175-200</td>
<td>Light yellowish grey (2.5Y 6/2), material lost from core (no sample)</td>
</tr>
<tr>
<td>200-255</td>
<td>Light brownish grey (10YR 6/2) silty clay with many medium areas of olive brown (2.5Y 4/4); 4cm diameter shell at 238cm; boundary change over 5cm width</td>
</tr>
<tr>
<td>255-285</td>
<td>Black (N 2/-) silty clay with shells and a pattern of unidentifiable fine lines</td>
</tr>
<tr>
<td>285-305+</td>
<td>Dark grey (10YR 4/1) silty clay with shell fragments and twigs; becoming extremely flinty below 300cm depth</td>
</tr>
</tbody>
</table>

3.1.2. Soil water content

The soil moisture content is the ratio of the volume of contained water in a soil compared with the entire soil volume. When a soil is fully saturated, water will drain easily into the underlying rocks. When this drainage stops, the soil still retains capillary moisture and is said to be at field capacity. If the soil dries further a soil moisture deficit is created, this is the amount of water which must be added to the soil to restore it to field capacity (Allaby and Allaby, 1999). The chemical interaction between the burial medium and an object buried within it is mediated largely by the chemical nature of the soil solution. Most chemical reactions require water so data regarding the water content
and water chemistry of burial soils and sediments is important for understanding chemical processes of degradation (Pollard and Heron, 1996). At Alice Holt the dipwells filled with water only when the soil was fully saturated, when it was not saturated the water did not move laterally and the dipwells remained dry. To provide data regarding the soil moisture content when the dipwells were dry, Forest Research installed soil moisture probes which were capable of recording levels of moisture in unsaturated soils.

The relationship between water levels and precipitation was also investigated and both high water level episodes and high rainfall patterns were identified. High water level episodes were defined as any sudden peaks in water levels and the precipitation levels for the days before and after these readings were examined. High precipitation episodes were defined as around 10mm or above in a day. The water levels were all compared to see if there was any correlation in the recorded water levels across all the dipwells. There are two instances when the results do not correlate. On 22nd June 2005 the water level was -0.25m below the ground in dipwell 1 (horizon 1) and 3 (horizon 3) however, dipwell 2 located in between these (horizon 2) did not record any water present. There was also no water present in any of the set of 2 dipwells on the other side of the burial trench. The second example was recorded on 11th January 2006 when the water in dipwell 3 (horizon 3) was recorded as being above the ground surface, yet no water was recorded in dipwells 1, 4 and 6 and the water level in dipwells 2 and 5 was only -0.438 and -0.357m below ground respectively.

There are a number of factors that could explain the differences in water level readings including, the incorrect installation of the dipwells which prevented the water level in the dipwell from reflecting the water table in the ground. It could also be that the
influence of the local geology affected the hydrological regime. The excavation, backfilling and compacting of such a large volume of soil (approximately 1.71m³) could have changed the hydrological regime by creating voids which altered the nature of the deposit. Soil moisture results for each of the burial horizons illustrated the range of percentage soil moisture at each depth. The highest range was at a depth of 100cm (67%) followed by 60cm (65%), 10cm (44%), 40cm (34%), 20cm (22%) and the lowest being 30cm (18%). This could have reflected the influences of precipitation on the uppermost 20cm and of groundwater on the lower depths (Graham et al., 2007).

The water contents of soils and sediments at Firestone were calculated to determine both spatial and temporal variations at the three monitoring stations. Samples were collected seasonally between 1999 and 2000 using a 50 cm gouge auger. The final sample sequence was removed in late summer of 2000 to allow comparison with summer samples taken the previous year. At the initial collection, undertaken on the fifth of August 1999, samples were removed only from the top and the base of the column (0-10 cm and 85-95 cm depth). Subsequently samples were taken at 0-10 cm, 45-55 cm and 85-95 cm depths. Samples were immediately triple-bagged on site, labelled and taken back to the laboratory and processed immediately after arrival. The samples were then oven dried for 24 hours at 105°C and results used to calculate the field water content. There was considerable seasonal variation in water content within individual profiles. At the near surface, this is likely to result from changes in the water balance between evapo-transpiration losses and precipitation inputs. At mid-depth summer decline of the water table may allow some drying out to take place. Within the deepest sample depth, variation in water content was more likely to be due to variation in soil/sediment porosity available to contain water at the point of sampling, since the water table did not decline to that depth during the study period. The mid-depth and
base samples showed water logging throughout the year. These levels are however less in both the late summer samples from 1999 and 2000. This may illustrate that the lower levels of precipitation and higher levels of evapo-transpiration do reduce the moisture content of the sediment in the summer. Daily rainfall figures, obtained from Newport were used to calculate antecedent rainfall over the previous 1, 3, 7 and 10 days prior to monitoring visits. Correlation analysis was used to investigate possible relationships between water level changes measured in 50 and 100cm piezometers, calculated since the previous visit, and antecedent rainfall. The results shown in Table 3.6 indicated that a significant relationship between rainfall and water table movement was found only at the 5% level, for P50 with 7 and 10 day rain periods. Values for P50 were always greater than P100 suggesting that the water levels at shallower depth are more likely to be reflecting responses to rainfall. Though not significant, P100 gave negative values with 7 and 10 day rain periods, suggesting further a lack of impact of recent rainfall (10 antecedent days) on the water table at depth (Hogan, et al., 2006).

Table 3.6 Results of correlation analysis between water levels and antecedent rainfall at the Firestone monitoring station

<table>
<thead>
<tr>
<th></th>
<th>Rain day 1</th>
<th>Rain day 3</th>
<th>Rain day 7</th>
<th>Rain day 10</th>
<th>P50</th>
<th>P100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rain day 1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rain day 3</td>
<td>0.677151</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rain day 7</td>
<td>0.608911</td>
<td>0.717491</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rain day 10</td>
<td>0.562032</td>
<td>0.582414</td>
<td>0.876025</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P50 change</td>
<td>0.079639</td>
<td>0.203339</td>
<td>0.302409</td>
<td>0.297962</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>P100 change</td>
<td>0.017436</td>
<td>0.058521</td>
<td>-0.14253</td>
<td>-0.05173</td>
<td>0.088676</td>
<td>1</td>
</tr>
</tbody>
</table>

n=56, significant values 0.259 (5%), 0.3362 (1%)

The samples recovered from Firestone are interesting in that the recorded levels of iron in the water recorded by monitoring are very low and staining may be related to the level of microbiological activity. It would be useful to experiment with new methods of
removing staining which would be less harmful to the materials. Perhaps this type of staining could be removed with biological agents rather than mechanical or chemical methods. The iron would be expected to be in a reduced condition at the freshwater and brackish wetland sites due to the nature of the burial environment. Iron can catalyse oxidation reactions in aqueous solution which are known to cause modification of amino acid side-chains and damage to polypeptides and can even cleave peptide bonds. This could be a factor in the deterioration of the horn samples. Heavy metals disrupt disulfide bonds because of their affinity and attraction for sulfur and eventually cause denaturation of proteins (Hermanson, 2008). In a previous study at Firestone (Hogan, et al. 2006) bacteria were examined from soil samples with facultative anaerobes being identified with a small number of anaerobic bacteria lower down in the sediment column.

At Fiskerton water levels were recorded monthly from August 2003 and the results for cluster 1 & 2 are illustrated up to March 2007. The proximity of cluster 1 to the delph did in effect mean that the drawdown effect of this drainage ditch had a significant influence on the levels. Levels recorded were between approximately 1.4m and 0.7m below the ground, but mostly varied little from 1m below ground. The average level for the cluster 1A peizometer was 0.98m below ground. There was a slight but recognisable difference in water levels following rewatering which occurred in October 2004, with averages before 1.17m and after 0.89m. Water levels in peizometres A and B were virtually identical.

Cluster 2 water levels were not influenced by the delph but did exhibit significant seasonally fluctuations, in the first year ranging from 1.6m below ground in November 2003, to 0.67m below ground in February 2004. After water levels were raised
following the installation of clay and stone bunds in the North – South aligned drainage ditches at either side of the field, the extremely low water levels stopped being recorded and the lowest level recorded after November 2004 was 0.88m below ground, with an average level of 0.44m. The installation of the bunds had an immediate effect on water levels which rose from 1.1m to 0.45m between October and November 2004.

Table 3.7 Seasonal variations in soil moisture content from the Alice Holt and Firestone sites. No data was available from Fiskerton or Alum Bay

<table>
<thead>
<tr>
<th>Sample depth (cm)</th>
<th>Seasonal changes of moisture content (%) at different sites</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Summer</td>
</tr>
<tr>
<td>0-10</td>
<td>22</td>
</tr>
<tr>
<td>35-55</td>
<td>56</td>
</tr>
<tr>
<td>85-100</td>
<td>98</td>
</tr>
</tbody>
</table>

The soil moisture data recorded at Alice Holt showed increasing moisture levels within the depths of the profile. The data also illustrates the lessening effect of seasonality with increasing depth of sediment. There is less variation in moisture content lower in the profile suggesting that the upper layers are more influenced by evapo-transpiration and precipitation whilst deeper in the profile groundwater is more influential.

Alice Holt is a terrestrial site where sample dampness increases with depth. Samples were buried at three different depths within the soil profile. The water chemistry at the different depths varied as did the level of the water in the piezometers. The water table exhibits seasonality, falling in summer and rising in winter. The moisture contents of the sediments at Firestone and at Alice Holt are shown in Fig.3.1.
The pattern of waterlogging is similar between Alice Holt and Firestone, with greater moisture content occurring with increasing depth of the sediment profile, however the terrestrial site had a higher moisture content generally. This is due to the fine grained nature of the sediment and bedrock. The smaller clay particles at Alice Holt enable the sediment to retain higher levels of moisture than the silts at Firestone.
3.1.3. Water Levels

The mean depth of water below the ground recorded at the three environmentally monitored reburial sites is illustrated in Table 3.8 and Fig. 3.2. The hydrological regime at the terrestrial site exhibited seasonal variation in that there was more water recorded in the dipwells in winter than in the summer. The shallow dipwells, 1 and 4, (38 cm) contained a small amount of water in the summer period and these events could be attributed to specific periods of rainfall. However, at other periods they remained dry indicating that the site was not permanently waterlogged at the depth at which some samples were buried. Similarly the deeper dipwells remained dry during the summer season but retained water during the winter. At the freshwater wetland the water levels were measured from piezometers at depths of 1.7 m (A) and 1.2 m (B). Before the land drains were blocked, the average water level at Cluster 1 was 1.15 m within a range of 0.67 to 1.62 m below ground level. After the land drains were blocked in October 2004 the water level rose, rising to 0.72 m below the ground surface.

The mean water level for the cluster 1 A piezometer was 0.99 m below the ground surface, whilst at piezometer B the mean water level was 1.10 m below the ground surface, showing that the samples remained waterlogged for much of the period. The environment was changed deliberately during the period of monitoring in an effort to protect waterlogged archaeological organic remains (Williams, 2005). There is evidence that fluctuations in the water table cause relatively rapid degradation of organic materials. The data comes from bone samples which were buried in the cluster 2 burial site. There was little change in the condition of collagen fibrils in any bone buried for six months, and for longer burial periods for those samples held in the top (exposed) and base (waterlogged) levels. In contrast to these minor changes, extensive alteration
was observed in the collagen fibrils of bones from the middle of the tube, which experienced a fluctuating water table. This degree of damage has previously been observed in bone which has been heated for several hours at 100 °C (Graham and Williams, 2008).

**Table 3.8** Mean depth below the ground surface of water at the three monitoring stations which produced data

<table>
<thead>
<tr>
<th>Site</th>
<th>sample</th>
<th>Mean depth (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alice Holt</td>
<td>1</td>
<td>-25</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>-37.17</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>-69.8</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>-75.25</td>
</tr>
<tr>
<td>Fiskerton</td>
<td>A</td>
<td>-99</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>-110</td>
</tr>
<tr>
<td>Firesone</td>
<td>50</td>
<td>-17</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>-76</td>
</tr>
</tbody>
</table>

**Fig. 3.2** Mean depth below the ground surface of water at the three monitoring stations which produced data, 1,4,3,6, Alice Holt, A, B, Fiskerton, 50, 100, Firestone
At the Firestone monitoring station the 50 cm and 100 cm depth piezometers recorded different values of water level, though there was some coincidence to the pattern of rise and fall. Mean levels are illustrated in Table 3.8. Water levels in the topsoil remained within 20 cm of the surface. Water levels measured in the 50 cm piezometer were found always to be higher than those in the 100 cm piezometer indicating the probability of downward piezometric pressure (Hogan et al., 2006). Also the pattern of water level fluctuations differed between the 50 cm and 100 cm piezometer. At shallow depth there was more short-term fluctuation (between bi-weekly records), probably in response to local rainfall events.

The site at Firestone was similar to Fiskerton in that it remained permanently waterlogged at the depth at which the samples were buried. The samples buried at Alice Holt would have been subject to periods of wetting and drying only the deepest would have remained at least damp for much of the burial period. The freshwater samples would have remained waterlogged but may have been affected by the raising of the water table during the burial period. It may be possible with further analysis to detect changes which may have been caused by the raising of the water table. The relative stability of the environment at Firestone, in respect of low Eh potential and neutral pH, would have reduced the risk of any sudden change in the samples. Degradation would take place at a more gradual and probably more predictable manner than at the other two sites. It is unfortunate that Alum Bay was not environmentally monitored as its waterlogged aerobic nature would have provided an interesting contribution for comparison with the other sites used in the study.

There is a need to quantify differences in measuring techniques and equipment to ensure that when the same parameters are monitored so that the answers obtained are not very
different. This would be possible at Alice Holt by quantifying differences obtained in data from piezometers compared to data from tension lysimeters located at similar depths in the profile. The monitoring devices at Alice Holt included soil moisture probes tension lysimeters and piezometers. The waterlogged sites were monitored with piezometers. These were generally bailed out and allowed to refill before sampling. It would be useful to compare how much the water monitored before bailing out the piezometers differed from that sampled and monitored after bailing and refilling.

3.2. Water Chemistry of the sites

The environmental monitoring data collected from the burial sites is examined below. The relevant data are analysed and compared to establish the nature of the burial environments in an effort to suggest which environments may be more protective to buried organic archaeological materials.

3.2.1. Eh Potential

Eh potential is an intensity measurement of the overall redox reaction potential in a system. This is the electrical potential generated between a platinum electrode and a standard hydrogen electrode when monitoring groundwater where hydrogen is considered the reference electrode (Vance, 1996). The voltage collected in the field must be corrected to the voltage which would have been obtained using the standard hydrogen electrode. This cannot be used in the field but values of Eh potential use it as a base. Therefore all voltages measured in the field with either silver chloride electrodes or calomel reference electrodes are corrected to the value which would have been obtained using a hydrogen reference electrode.

Field Voltage + Correction Factor = Redox Potential (Eh) (Verpraskas, 2002).
The redox potential at Firestone and latterly at Fiskerton were measured with a calomel cell and the readings were calibrated. Readings taken at Alice Holt and originally at Fiskerton with an oxygen reduction probe were already calibrated to the standard hydrogen electrode, therefore the data recorded at each site could be compared.

At the Alice Holt site only the deeper dipwells numbers 3 and 6 contained enough water to take regular readings. The mean readings of both of these dipwells showed them to be moderately reducing and at the minimum levels recorded during the period they remained reduced. Eh potential measured via water collected from piezometers A and B at Fiskerton did not change significantly as a result of rewetting, but was influenced by changes in water availability resulting from seasonal fluctuations. When water levels were at their highest, Eh potential was also high and the lowest readings mainly occur during the driest months. It would appear that greater instability in the lower levels that are monitored occurs during periods of change when the site is very wet (Williams, 2005). This possibly results from the greater movement of water through the site during these periods. The mean readings of Eh potential recorded are illustrated in Fig. 3.3. Although the levels fluctuated greatly during the monitoring period, the deeper piezometer A showed greater reduction levels than those recorded for the shallower piezometer B with a more reduced Eh potential level of -36mV. This would suggest that the sediments are more reduced at greater depth. At the depth at which the samples were buried, the Eh potential could be classified as reducing for the majority of the monitoring period occasionally moderately reducing according to the scheme adopted for use in this study (Cronyn, 1990). At Firestone the response to hydrological regime in terms of Eh potentials indicated that the most oxidised conditions occurred consistently within topsoils where a seasonal draw-down of the water table takes place. Water levels
in the topsoil often remained within 20 cm of the surface with Eh potential there indicating slightly or occasionally moderately reduced conditions. Eh potential was generally moderately reduced (+100 to -100 mV) while subsoil/substrate Eh potential varied between moderately and highly reduced (-100 to -300 mV).

Fig. 3.3 Mean levels of Eh recorded at Alice Holt (4, 3 and 6), Fiskerton (sites A and B) and the Firestone site at depths of 50 and 100 cm. The site at Alice Holt at all monitored depths is the least reduced, Fiskerton the next least reduced and Firestone the most reduced.

The most reduced figure was recorded at Firestone (100 cm piezometer, -207 mV), the least reduced figure was recorded at the terrestrial site (90 cm dipwell +195 mV). The mean recorded levels suggest that the terrestrial site is the least reduced followed by the freshwater wetland with the brackish wetland generally being the most reduced of the recorded sites.

3.2.2. pH

At Alice Holt, the pH levels varied between slightly acidic to moderately alkaline. The greatest pH range was recorded in dipwell number 6 a range of around 2 pH units. The minimum recorded level was 6.2 and the maximum recorded 8.2. Mean levels of recorded pH at the monitoring stations are shown in Fig 3.4. Before the land drains were blocked in October 2004 at Fiskerton the mean pH at the Cluster 1 burial site was 6.5 at
a depth of 1.7 m within a range of 6.1-6.8, with a mean pH of 7.3 at 1.2 m a range of 2.6. After the land drains were blocked the mean pH at both depths remained virtually the same. It became slightly less acidic at 1.7 m depth, 6.5 and range of 0.7 and slightly more acidic at 1.2 m a range of 0.9 suggesting that raising the water table had reduced the fluctuations in pH between the two piezometers.

Measurements of pH at Firestone indicate that the values from the 50 cm piezometer were slightly lower than those from 100 cm depth probably due to the influence of alkalinity caused by the influence of tidal conditions at lower depths within the sediment. The minimum recorded level of pH was 5 and the maximum recorded level was 7.8. On average Alice Holt had the highest mean pH at 7.6 with Firestone next at 7 with Fiskerton having the lowest mean pH at 6.5.
Fig. 3.4 Mean levels of pH recorded at the monitored sites. Alice Holt consistently shows the highest level of pH with Firestone generally the lowest levels and Fiskerton in between.

The classification of the sites according to their mean pH levels is illustrated in Table 3.9. Alice Holt is mostly pH neutral but slightly alkaline at the number 4 dipwell. The Fiskerton site is classed as slightly acidic and Firestone as pH neutral (Fitzpatrick, 1986). The marine site although it was not monitored would be expected to be slightly alkaline which is normal for sea-water except in estuaries where it might be lower (Florian, 1987).
Table 3.9 Classification of mean pH recorded at the monitored burial sites

<table>
<thead>
<tr>
<th>Site</th>
<th>Sample</th>
<th>Mean</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alice Holt</td>
<td>1</td>
<td>6.9</td>
<td>Neutral</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>7.6</td>
<td>Slightly alkaline</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>7.0</td>
<td>Neutral</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>6.9</td>
<td>Neutral</td>
</tr>
<tr>
<td>Fiskerton</td>
<td>A</td>
<td>6.3</td>
<td>Slightly acid</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>6.5</td>
<td>Slightly acid</td>
</tr>
<tr>
<td>Firestone Copse</td>
<td>50</td>
<td>6.6</td>
<td>Neutral</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>7.0</td>
<td>Neutral</td>
</tr>
</tbody>
</table>
3.2.3 Eh/pH Relationship

The mean levels and site classifications of Eh and pH at each of the monitored burial sites are illustrated in Table 3.10.

**Table 3.10 Eh/pH, mean levels and site classifications**

<table>
<thead>
<tr>
<th>Site</th>
<th>Piezo.</th>
<th>Mean pH</th>
<th>Classification</th>
<th>Mean Eh (mV)</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alice Holt</td>
<td>1</td>
<td>6.9</td>
<td>Neutral</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>7.6</td>
<td>Slightly alkaline</td>
<td>+152</td>
<td>Moderately reducing</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>7.0</td>
<td>Neutral</td>
<td>+135</td>
<td>Moderately reducing</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>6.9</td>
<td>Neutral</td>
<td>+125</td>
<td>Moderately reducing</td>
</tr>
<tr>
<td>Fiskerton</td>
<td>A</td>
<td>6.3</td>
<td>Slightly acid</td>
<td>-36</td>
<td>Reducing</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>6.5</td>
<td>Slightly acid</td>
<td>-5</td>
<td>Reducing</td>
</tr>
<tr>
<td>Firestone Copse</td>
<td>50</td>
<td>6.6</td>
<td>Neutral</td>
<td>-64</td>
<td>Reducing</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>7.0</td>
<td>Neutral</td>
<td>-91</td>
<td>Reducing</td>
</tr>
</tbody>
</table>

Key: - no data

When the Eh is plotted against pH for piezometer no 6 at Alice Holt it can be seen that the environment at this depth is variable in both parameters. It is most regularly moderately reducing and slightly alkaline. When Eh is plotted against pH for Fiskerton, it becomes apparent that for the majority of the monitoring period the conditions at the burial site were slightly acidic and reducing with occasional fluctuations to less acidic reducing conditions. At Firestone the environmental conditions were generally close to
neutral pH and were reduced. The relationship between Eh and pH at each of the monitored burial sites is illustrated in Fig. 3.5.

**Fig. 3.5** Mean levels of Eh plotted against mean levels of pH for the monitored sites, Alice Holt (top), Fiskerton (centre), Firestone (bottom), all from 100 cm or closest equivalent depth
Firestone is consistently the most reduced of the monitored sites with a neutral pH. This would suggest using the criteria described by Watkinson (1987) Table 1.1, that this site would be the most protective for organic archaeological materials.

### 3.2.4. Conductivity and ion content

The mean, maximum and minimum levels of conductivity were recorded at specific time intervals from the three sites where monitoring took place. As well as conductivity levels, the mean, maximum and minimum levels of other ions which were thought to be significant in the environment were also monitored and recorded.

Additional data regarding the chemical composition of the groundwater Fiskerton was obtained from a 1.5L water sample abstracted from piezometer number 2 at the Cluster 2 monitoring station. The additional data used in the following section was taken from piezometer 6 at Alice Holt, dipwell B at Fiskerton and from the 100 cm piezometer at the Firestone monitoring station.

The levels of conductivity and number of ions in solution were examined from each of the sites and compared to the levels which are generally expected in ground water or sea water to explore how great the variations might be and to suggest what effect this may have on the buried samples. The results can be seen in Fig. 3.6.

At the Alice Holt monitoring station conductivity levels were relatively low with the maximum level recorded being 616 µS/cm which is slightly above the recommended level for drinking water which is 500 mg/L (Harter, 2003). Mean levels were recorded at 348 µS/cm with a minimum recorded level of 203 µS/cm.
At Fiskerton the maximum recorded conductivity level was 2770 µS/cm with the minimum recorded level being 1400 µS/cm. The mean level recorded was 2421 µS/cm. The increasing level of conductivity with depth is illustrated by the higher conductivity levels recorded at the deeper piezometer A. At the Firestone monitoring station the mean values of electrical conductivity were all in the strongly saline category, exceeding 15,000 µS/cm at both 50 and 100 cm depths for the majority of the monitoring period. The maximum recorded level of conductivity was 44,500 µS/cm at the 100 cm piezometer with a minimum recorded level of 32,300 µS/cm and a mean level of 39162 µS/cm. These high levels and also the large fluctuations in levels are the result of the sites location within the flood plain of a tidal estuary and reflect the influence of the sea on the groundwater system. The conductivity levels also increase with depth as they do at the other two monitored sites.

The site at Alice Holt has generally the lowest levels of conductivity with Fiskerton the next highest with Firestone having the highest recorded levels of conductivity. Firestone and the Alum Bay site have high levels of conductivity. Firestone forms part of a tidal estuary and conductivity levels are high, closer to marine conditions than they are to freshwater levels. High levels of soluble salts can cause significant damage to objects. They expand as the material dries and physically disrupt the structure and can cause complete disintegration. Consequently materials from contexts with high levels of salts should be desalinated prior to drying (Robinson, 1998). This would include samples of all the buried materials which have been buried and retrieved from Alum Bay and Firestone.

At the Alice Holt monitoring station the maximum recorded chloride level was 164.9 mg/L with a minimum recorded value of 22.4 mg/L and a mean value of 83.5 mg/L.
Fig. 3.6 Mean conductivity and levels of ions recorded at the three monitored sites

Key: 3,6, piezometers at Alice Holt, A,B,P2 piezometers at Fiskerton, 50, 100, piezometers located at Firestone

Chloride levels found within natural groundwater occur generally between limits of 1-1,000 mg/L so the Alice Holt site values are well within normal levels. At the Fiskerton
monitoring station the maximum recorded chloride level was 75 mg/L with a minimum recorded value of 34.4 mg/L and a mean value of 56.8 mg/L. At the Firestone monitoring station the maximum recorded chloride level was 22506.2 mg/L with a minimum recorded value of 14219.2 mg/L and a mean value of 19011.6 mg/L. The extremely high chloride levels recorded at the Firestone monitoring station reflect the saline nature of the estuarine system, with levels particularly at 100 cm depth close to levels which could be expected to occur in sea-water.

At the Alice Holt monitoring station the maximum recorded level of sodium was 80 mg/L with a minimum recorded value of 20.3 mg/L and a mean value of 47.3 mg/L. Sodium levels found within natural groundwater occur generally between limits of 1 - 1,000 mg/L so the Alice Holt values are well within normal groundwater levels. Fiskerton had no recorded values for the level of sodium. At the Firestone monitoring station the maximum recorded level of sodium was 7845.9 mg/L with a minimum recorded value of 424.4 mg/L and a mean value of 6744.9 mg/L. Sodium levels were high, more reminiscent of sea-water rather than groundwater. The large fluctuations also indicate the influence of tidal conditions on the water chemistry.

At the Alice Holt monitoring station the maximum recorded sulfate level was 36.9 mg/L with a minimum recorded value of 5.8 mg/L and a mean value of 18.5 mg/L. Sulfate levels found within natural groundwater occur generally between limits of 1 - 1,000 mg/L so the Alice Holt levels are low, well within expected groundwater values. At the Fiskerton monitoring station the maximum recorded level of sulfate was 1520 mg/L with a minimum recorded value of 656 mg/L and a mean value of 1023.4 mg/L. Sulfate levels were initially high when monitoring began at over 1500 mg/L but they fell steadily over the monitoring period to below 800 mg/L which is still quite high but
within the expected levels of natural groundwater. This reduction may have been the result of rewatering. At the Firestone monitoring station the maximum recorded level of sulfate was 1634.4 mg/L with a minimum recorded value of 1135.2 mg/L and a mean value of 1367.2 mg/L. Sulfate levels were high for groundwater but within expected levels for sea-water with fluctuations caused by the tidal nature of the estuary.

At the Alice Holt monitoring station, the maximum recorded level of iron was 433 mg/L with a minimum recorded value of 0 mg/L and a mean value of 164.5 mg/L. Iron levels found within natural groundwater occur generally between limits of 0.01-10 mg/L so the Alice Holt values were higher than usual groundwater limits. At the Fiskerton monitoring station, the maximum recorded level of iron was 43.9 mg/L with a minimum recorded value of 9.4 mg/L and a mean value of 22.2 mg/L these levels are lower than the Alice Holt site but still slightly higher than those expected to occur in groundwater.

At the Firestone monitoring station, the maximum recorded level of iron was 1.1 mg/L with a minimum recorded value of 0.1 mg/L and a mean value of 1.1 mg/L. These are low levels for groundwater but slightly higher than levels usually found in seawater. Iron levels were particularly high at Alice Holt and higher than would normally be expected in ground-water at the Fiskerton site.

These high levels of iron could have implications for degradation. The oxidation and reduction of iron in natural environments is extensively promoted by microbial catalysis so high levels of microbes and iron will facilitate these reactions. Iron species adsorb and precipitate compounds within the environment. One of these reactions is the binding of phosphate to iron oxides. In the natural environment this regulates the release of nutrient from sediments, (Canfield et al., 2005). Significant iron staining was observed on a number of antler and ivory samples indicating that environmental iron
may be bonding to the phosphate within the material. This has been noted previously on ivory samples from an excavated marine site (Tripati and Godfrey, 2007). Generally in marine settings iron staining is caused by the material being buried near to rusting iron objects. It is a problem for conservation as the chemically bound iron is very difficult to remove from an object without causing damage to the substrate. The usual chemical means of cleaning these stained objects is by the use of chelating agents such as disodium EDTA which is potentially harmful to objects as it breaks down the polypeptide chains within the protein component of the materials.

On visual inspection antler and ivory samples appeared to be more heavily iron stained than the horn samples indicating that the mechanism outlined above regarding phosphate binding to iron oxides may be prevalent. Samples which showed observable iron staining were recovered from all of the sites. It appeared to be much less on the horn samples and increased with increasing burial time. The samples recovered from Alum Bay and Firestone appeared to be the most heavily stained and they had the longest burial period.

3.3. Evaluation of environmental data

The burial environment is not static, it is a complex system where parameters fluctuate and change. In order to see whether these fluctuations were of significance in regard to the samples recovered from the burial sites a simple statistical analysis was carried out on the two most significant environmental factors within the environment for the preservation of archaeological materials Eh and pH

A statistical method of the measurement of fluctuation is variance:

\[ \text{Variance} = \frac{(x - \text{mean})^2}{(n -1)} \]

Where x is the observed value and n is the number of observations.
If the mean is known each recorded value can be subtracted from it then squared so that the answer becomes positive. If these ‘mean square deviations’ are added together and divided by the number of observations this is the variance. The square root of the variance is the standard deviation. This will provide information about how far from the mean figure the Eh and pH vary at each site allowing comparisons to be made between sites. This was done to establish whether sites exhibiting greater fluctuations in environmental chemistry proved to be more degrading to archaeological materials than those where the environment fluctuated less. The calculation of variance gives an impression of the dynamism within the differing burial environment. These fluctuations can then be compared between the sites by using the variance to calculate the number of standard deviations from the mean of each parameter.

There are fluctuations in the levels of most of the environmental parameters measured at all of the sites and between samples from different depths. These fluctuations may be significant in relation to material degradation. The mean variations in Eh and pH values for the burial sites were recorded. The burial environment is considered to be more preserving the more reduced it becomes. The recorded fluctuations from the mean in Eh potential and pH are illustrated in Table 3.11. The lowest mean Eh potential was recorded at Firestone, with Fiskerton the next lowest and Alice Holt the least reduced.
Table 3.11 Range and mean of Eh potential recorded at the monitored burial sites

<table>
<thead>
<tr>
<th>Site</th>
<th>Sample Location</th>
<th>Min</th>
<th>Mean</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alice Holt</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>23</td>
<td>135</td>
<td>184</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>36</td>
<td>125</td>
<td>195</td>
</tr>
<tr>
<td>Fiskerton</td>
<td>A</td>
<td>-199</td>
<td>-36</td>
<td>161</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>-133</td>
<td>-5</td>
<td>159</td>
</tr>
<tr>
<td>Firestone Copse</td>
<td>50</td>
<td>-166</td>
<td>-64</td>
<td>182</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>-207</td>
<td>-91</td>
<td>148</td>
</tr>
</tbody>
</table>

When the standard deviation from mean recorded levels is examined, shown in Table 3.12, the differences become clear. Whilst the Firestone site is the most reduced it also shows the greatest range between data illustrating a wide degree of fluctuation. At this site this may be caused by the influence of the tide and the influence of precipitation which causes the site to become less reduced (Hogan et al., 2006). The 50cm deep piezometer is generally less reduced than the 100cm deep piezometer. However even the maximum levels are still in the moderately reducing category. Similarly Fiskerton has fluctuations which may also be related to the influence of precipitation and groundwater movement and possibly the raising of the water table (Williams, 2008). The Alice Holt site is the least reduced but also has the least variation.
Table 3.12 Standard deviation of Eh potential recorded at the monitored burial sites

<table>
<thead>
<tr>
<th>Site</th>
<th>Sample Location</th>
<th>Standard Deviation</th>
<th>Mean Eh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alice Holt</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>57.32</td>
<td>135</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>45.05</td>
<td>125</td>
</tr>
<tr>
<td>Fiskerton</td>
<td>A</td>
<td>67.20</td>
<td>-35.71</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>65.19</td>
<td>-5</td>
</tr>
<tr>
<td>Firestone Copse</td>
<td>50</td>
<td>98.65</td>
<td>-64</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>108.18</td>
<td>-91</td>
</tr>
</tbody>
</table>

The standard deviation from the mean figure of Eh was greatest at the Firestone site and least at Alice Holt. Firestone is the most reduced in terms of Eh but also fluctuates more than the other sites. This may well be caused by the influence of the tide.

The ranges in the levels of pH at the monitored burial sites are illustrated in Table 3.13. The highest level of pH was recorded at the Fiskerton site at 8.6, the lowest recorded figures were from Firestone at a pH of 5. The sites were classified by using the mean figures as Alice Holt, slightly alkaline, Fiskerton, slightly acidic and Firestone, neutral. The site showing the widest range in mean levels of pH was Alice Holt. The smallest fluctuations occurred at Fiskerton though the figures for Fiskerton and Firestone were reasonably similar.
### Table 3.13 Maximum, minimum and mean levels of pH at the monitored burial sites

<table>
<thead>
<tr>
<th>Site</th>
<th>Sample</th>
<th>Min</th>
<th>Mean</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alice Holt</td>
<td>1</td>
<td>N/D</td>
<td>6.9</td>
<td>N/D</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>7.5</td>
<td>7.59</td>
<td>7.7</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>6.52</td>
<td>7.02</td>
<td>7.8</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>6.18</td>
<td>6.85</td>
<td>8.16</td>
</tr>
<tr>
<td>Fiskerton</td>
<td>A</td>
<td>6.09</td>
<td>6.63</td>
<td>7.74</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>6.05</td>
<td>6.46</td>
<td>8.61</td>
</tr>
<tr>
<td>Firestone Copse</td>
<td>50</td>
<td>5.23</td>
<td>6.62</td>
<td>7.62</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>4.96</td>
<td>6.96</td>
<td>7.84</td>
</tr>
</tbody>
</table>

As pH is measured on a logarithmic scale each change represents a considerable difference in the concentration of dissolved hydrogen ions and may be significant regarding the preservation or deterioration of materials. The standard deviation of pH levels at each burial site was calculated and the results shown in Table 3.14. In all three sites the standard deviation from mean levels increased with depth showing that there is more fluctuation in pH levels deeper within the burial environment. At depth the differences between sites were small with Fiskerton showing slightly less deviation overall.
Table 3.14 Standard deviation of pH at the monitored burial sites

<table>
<thead>
<tr>
<th>Site</th>
<th>Sample</th>
<th>Standard Deviation</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alice Holt</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.40</td>
<td>7.02</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.63</td>
<td>6.85</td>
</tr>
<tr>
<td>Fiskerton</td>
<td>A</td>
<td>0.32</td>
<td>6.63</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>0.51</td>
<td>6.46</td>
</tr>
<tr>
<td>Firestone Copse</td>
<td>50</td>
<td>0.53</td>
<td>6.62</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.60</td>
<td>6.96</td>
</tr>
</tbody>
</table>

According to the categories used in the study (Cronyn, 1990), Alice Holt can be classified as slightly reduced and slightly alkaline. Fiskerton can be classified as slightly reduced and slightly acidic and the Firestone site as moderately reducing and neutral. In these particular types of environment it may be expected that Firestone would be the site with an environment most likely to preserve all of the materials. Horn could possibly survive at Fiskerton due to its slightly acidic mean pH which would be detrimental to the survival of antler and ivory. The Alice Holt site should preserve antler and ivory better than the horn, whilst the Alum Bay site would preserve antler and ivory due to its high calcium carbonate content and slight alkalinity. All of the sites are either waterlogged or damp. This would mean that all of the materials would be likely to suffer physical damage as they dried out. These drying stresses would be exacerbated at
Alum Bay and Firestone with the high levels of conductivity causing salt penetration of the materials. Unless salts are removed they will expand as the materials dry increasing the amount of physical deterioration. Firestone would be expected, looking at mean figures, to be the most protective of the burial environments examined in the study. However it did also have the greatest deviation in terms of Eh potential.
CHAPTER 4

DEGRADATION OF IVORY, ANTLER AND HORN

4. Introduction

The organic materials studied - horn, antler and ivory - are materials which were used extensively by man in antiquity (MacGregor, 1984). The materials degrade physically, chemically and biologically, the nature and rate of deterioration being dependent on the burial environment.

4.1. Preservation in situ Rationale

According to the categories used in the study (Watkinson, 1987, Cronyn, 1984), the site at Alice Holt can be classified as slightly reduced and slightly alkaline. At Fiskerton the site could be classified as waterlogged, reduced and slightly acidic according to the criteria adopted. The site at Fiskerton was at the time of the study being rewatered to improve the preservation of organic archaeological remains. In its altered state preservation should be improved. In these conditions, the survival of horn would be possible whilst the deterioration of antler would be greater.

Antler and ivory do not survive well in acidic environments as acidic conditions dissolve the mineral component hydroxyapatite. These materials could be considered unlikely to survive in these conditions. Finally, the site at Firestone would be classified as waterlogged, neutral and moderately reducing. Interestingly all of the types of sample material would only be expected to survive in a waterlogged environment with a neutral pH, such as that found at Firestone. This type of environment is also likely to preserve
other types of organic material particularly waterlogged archaeological wood (Hogan, *et al.*, 2006). Horn is unlikely to survive in waterlogged environments in the long term as the rate of hydrolysis increases in these conditions as peptides are broken down into amino acids, however ivory and antler may survive, (Cronyn, 1990). A waterlogged slightly alkaline environment such as that at Alum Bay would increase the rate of hydrolysis of proteins. This type of environment is that which would be expected at Alum Bay. The minimal hydraulic conductivity at Alice Holt may also favour the preservation of organic materials by limiting the numbers of aerobic bacteria but this must be tempered with the risk of mineral deterioration. This is illustrated by experiments conducted by Forest Research (Crow, 2008). At Fiskerton deterioration of antler was slow as the samples were buried below the water table even before the water levels were raised. However bone samples which were buried higher in the sediment were rapidly degraded probably due to fluctuations in the water table as changes were taking place. This is important it stresses that for a site to be protective it requires a stable water table.

The following section examines the amount and type of degradation which each of the materials had experienced at each of the burial sites and investigates whether they behave in reality as predicted by the prevalent environmental conditions at each site. The burial periods were relatively short so it was unlikely that any of the materials would be totally degraded The analytical data was compared with the predicted behaviour of the materials described by Watkinson in Table 1.1(page 8) and by English Heritage illustrated in Fig. 1.1(page 24). The analysis illustrated whether or not horn, antler and ivory were suitable materials for preservation *in situ* in the burial environments which were studied.
4.2. Experimental Methods

Six different methods of scientific analyses were undertaken on samples which had been buried and recovered from the four burial sites in the course of this study. The analytical techniques were selected to provide a wide range of information on the deterioration of the materials chemically, mechanically and biologically in order to better understand the nature and rate of decay within the environments where they had been buried and subsequently retrieved over various periods of time. Weight loss was selected as a technique which provides an overview of the general deterioration of materials and it is a relatively simple technique to carry out. Scanning Electron microscopy was used to examine the surfaces of the samples to observe whether any physical changes occurred on the samples recovered from the burial sites. The Scanning Electron Microscope also has high enough levels of magnification to show any bacteria which may have been present on the surfaces. The SEM was used in conjunction with Electron Probe Micro-analysis. This analytical technique was used to identify the proportions of different elements on the surfaces of the samples. Additionally the microprobe shows changes in the number and type of elements on the surface, therefore illustrating whether elements were lost into or gained from the burial environment by the recovered samples. Unfortunately the microprobe used in the study did not have the capability of measuring the amount of increase or decrease in the surface elements. Newer systems however do have this capability and any future research would benefit from being able to quantify these changes. Fourier Transform Infra-Red Spectroscopy has been used extensively in the examination of organic materials. In this study it was used to determine the relative amounts of collagen and keratin in the samples and to analyse the amount of sample degradation. In the cases of the antler and ivory samples it was also used to assess the
changing proportions of deterioration between the protein component and the mineral fraction of these materials. X-Ray Diffraction Spectrometry was chosen as an analytical tool to examine the crystal structures of the materials in order to establish whether any changes were taking place and to establish whether new crystals may have formed or been deposited on the sample surfaces. This technique was not useful for examining the horn samples which have no crystal structure but it did prove interesting in looking at changes which took place on some of the recovered antler and ivory samples. Biological analyses were undertaken to establish whether samples were being degraded by microorganisms. It was felt that the proteins would be attacked by protein degrading bacteria and fungi. Only collagen degrading proteases were tested for during the analysis. The enzyme which was used in the experiments was known to degrade keratin (Burtt and Ichida, 1999), therefore it was felt that it was unnecessary to test for it. If horn samples had been used in the experiments it was felt that keratin degrading bacteria would have been identified and also possibly fungi particularly Actinomycetes.

It was felt that by using a multi-analytical approach to material evaluation a picture of types and rate of degradation would be achieved and also possible relationships between types of deterioration might be identified.

4.2.1. Weight Loss

Weight loss measurement was used as a method of showing the general level of overall deterioration in all of the types of sample material buried and recovered at various time intervals from the reburial study sites. Samples which had been recovered were weighed and then oven dried. The differences in weight were then calculated and used as a measure of the degradation which had taken place in the samples. Although this
technique is useful for sample material it cannot be used on recovered archaeological material as the original weight would be unknown. All of the retrieved samples which were used in the weight loss calculations were first washed in running water and brushed to remove loosely adhering silts prior to heating in a laboratory oven for 24 hours at 105°C. They were then weighed on an LB 300 electronic laboratory balance. Weight loss was calculated using the formula

\[
\frac{(\text{Initial oven dry weight} \ - \ \text{Final oven dry weight}) \times 100}{\text{Initial oven dry weight}}
\]

4.2.2. Scanning Electron Microscopy (SEM)

Before viewing samples were dried in solvent baths. The dried samples were then mounted onto carbon stubs using carbon cement as adhesive and then coated with a thin layer of gold in a vacuum chamber to prevent the build up of an electrical charge on the surface of the sample. These analyses were undertaken using a JEOL 6100 Scanning Electron Microscope operated at 25 kV, coupled with a Link Analytical EDAX facility. These were located in the Earth Sciences Department at Portsmouth University.

4.2.3. Electron Probe Micro-Analysis (EDAX)

The EDAX samples were prepared in the same manner as the samples used in the SEM however they were not generally coated with gold. Coating the samples with gold slightly reduces the sensitivity of the analysis. One gold coated sample was used as there was no uncoated sample available and the gold did appear on the analytical chart. Analyses illustrate the semi quantitative elemental composition of the first 3-5 microns on the surface of the sample. This is highly significant when looking at the interaction
of a sample with its burial environment, any new elements bonding to the surface or elements leaching out of the sample into the environment should be observed in the micro-probe results. The electron beam was targeted using the SEM so that specific spots on the sample could be analysed. The results are expressed in charts which show the relative proportions of elements on the surface of the sample.

4.2.4. Fourier Transfer Infra–Red Spectroscopy (FTIR)

Fourier Transform Infra red Spectroscopic analysis was undertaken using a Perkin Elmer Spectrum 100 Fourier Transform Infrared Spectroscoper, (FTIR) located at the Mary Rose Trust in Portsmouth. A scan range of 4000-650 cm\(^{-1}\) was employed, with a wave number resolution of 4 cm\(^{-1}\) and scan accumulation of 32. The samples were prepared by abrading the material against silicon carbide paper. For comparative purposes the spectrum of fresh antler, ivory and horn were also scanned.

The ratios and intensities of the peaks were produced in a standard format to allow comparisons to be made. This was achieved in this study by using facilities available in the software of the spectrometer. Spectra were first smoothed and processed then normalised to produce spectra which could be directly compared.

4.2.5. X-Ray Diffraction Spectrometry

The XRD analysis was undertaken at English Heritage, Fort Cumberland, Portsmouth on a Philips 1830 / 1840 X-ray diffractometer with a Cobalt anode. The samples were ground using an agate pestle and mortar, sprinkled onto a glass slide and industrial methylated spirits dropped on to evenly disperse the sample. The XRD analysis was undertaken at English Heritage at Fort Cumberland, Portsmouth on a Philips 1830 / 1840 X-ray diffractometer with a Cobalt anode. X-rays of a known wavelength were
fired at the sample. The amount of radiation was measured and the results entered into a computer which had a reference section of crystal structures. The samples’ diffraction patterns were then compared with the reference spectra to identify the sample.

The peaks were identified using the X-Pert High Score Square software (Version 2.0, 2005): each scan was run against the International Centre for Diffraction Data (ICDD) database of Powder Diffraction Files (PDF) with a restrictions file in place to narrow the search on the samples corrosion products and minerals. Each scan was then checked to determine if there was a good match between the peaks in the scan and the PDF d-spacings. Further PDFs were manually inputted to determine potential matches for example, soil minerals.

4.3. Weight Loss

4.3.1. Alice Holt

At Alice Holt, horn and antler samples were buried at three different recorded depths, commensurate with three distinct recorded soil horizons. Additional samples were exposed to the atmosphere and a final group placed approximately 3 cm below the surface of the leaf litter. Samples were only left exposed and in the leaf litter for 6 months. There are no 20-month comparisons to be made with these two groups. In any future studies it would be interesting to leave samples exposed and in the leaf litter for longer periods to allow biostratinomic processes to be investigated and compared with samples recovered from specific burial horizons. There are variations in the percentage of weight loss which took place between different materials recovered at different time periods from different burial horizons. The lowest weight loss in antler samples recovered after six months and twenty months of burial took place in samples buried in
Horizon 3 whilst the highest mean weight loss of horn samples recovered after similar burial periods was recorded in samples recovered from Horizon 3. This may suggest that the differences in the materials are responsible for different reaction rates and processes of deterioration within this particular Horizon.

**Antler**

The exposed antler samples deteriorated slightly less than the buried ones. However after 6 months there were marked differences in the weight loss between the exposed antler and horn samples. The exposed antler samples deteriorated slightly more than the horn but less than the buried ones. This might suggest in the short term that exposed samples are subject to less chemical and biological degradation.

General trends were as expected, the samples buried for 20 months deteriorated more than the ones buried for 6 months. There is an anomaly in the 6 months buried antler sample from Horizon 1 where one of the samples exhibited an extremely high level of weight loss. This may be related to an as yet unidentified process or may be related to a localised micro environment within the site. A potential explanation lies within the nature of the physical structures of the samples themselves. Antler is similar in composition to bone and would therefore be expected to deteriorate in a similar manner (Collins, 1995). However antler is physically denser externally than it is internally. The internal structure is highly porous to accommodate the blood vessels necessary to allow its rapid growth. It is likely that samples with a greater area of exposed internal structure will deteriorate more quickly than those which contain a higher proportion of the external wall. Its greater porosity will lead to more rapid exposure to the conditions prevalent within the burial environment.
The weight loss of antler samples at the Alice Holt site is illustrated in Fig. 4.1. The highest recorded level of weight loss occurred in antler sample S12 buried in soil horizon 1 which was recovered after a burial period of 20 months with a weight loss of 30%. Interestingly the lowest recorded was the sample left exposed for 6 months, S16 weight loss 16.1%.

![Fig. 4.1 Weight loss of antler samples recovered from the Alice Holt burial site after 6 months (blue) and 20 months (red) burial periods](image)

Key to burial location E; (exposed), L; (leaf litter), H1; (Burial Horizon 1), H2; (Burial Horizon 2), H3; (Burial Horizon 3)

**Horn**

The exposed horn samples deteriorated least of all, followed by the horn samples which were buried in the leaf litter. The maximum recorded weight loss in the horn samples occurred in S1 buried in soil horizon 3 and retrieved after 18 months with a weight loss of 28.4%. The lowest recorded weight loss in the horn samples occurred in sample S13, which was not buried but left exposed by suspending it on a post on the site for 6 months. The weight loss of horn samples at Alice Holt is illustrated in Fig. 4.2.

It is interesting to note that the largest amount of degradation within the samples occurred within the first six months of burial and that deterioration in both antler and horn samples slowed considerably between burial after 6 months and 20 months.
Horizons 1 and 3 showed higher levels of recorded weight loss than the other locations. The antler samples exhibit greater variation in the amount of recorded weight loss. The horn samples exhibited the greatest levels of deterioration and greatest increase over time.

Fig. 4.2 Weight loss of horn samples recovered after 6 months (blue) and 20 months (red) burial periods at the Alice Holt burial site

Key to burial location E: (exposed), L: (leaf litter), H1: (Burial Horizon 1), H2: (Burial Horizon 2), H3: (Burial Horizon 3)

It is possible that the horn samples are more degraded due to hydrolysis and the activities of fungi and bacteria in the higher levels and by hydrolysis in the deeper horizon. The antler samples are less degraded deeper in the soil horizons probably due to a lack of water movement and no biological activity. A previously undertaken study examined the deterioration of various minerals within the burial environment (Graham and Crow, 2010). One of the minerals studied was apatite which is very similar in composition to hydroxyapatite the mineral component of antler and ivory. The laws of thermodynamics dictate that the reference material will lose ions into the surrounding environment until they reach equilibrium with that environment. The rate at which ions are removed and the level at which the concentration of ions are diluted will be determined by the level of soil water movement. A high rate of water exchange
removing dissolved ions will mean that the reference minerals cannot reach equilibrium with its surrounding environment and will continue to deteriorate. Saturation Indices (SIs) derived from the data from the monitoring sites were plotted against the actual quantities of reference sample lost. Saturation Indices of zero indicate equilibrium between the soil solution and the solid mineral. A negative index illustrates the active dissolution of the mineral into solution and a positive index shows active precipitation of the mineral out of solution. Fig. 4.3 illustrates the SIs for apatite monitoring points at the Alice Holt monitoring station. The negative indices relating to apatite suggests that the soil solution at all levels of the site and surroundings would lead to its loss.

The predicted loss of the model and the actual percentage loss of mineral were in reality quite close over a 5 year period of monitoring at this site. Geochemical modelling was undertaken using a computer programme, (Phreeqci), developed for the United States Geological Survey. The programme uses soil solutions obtained from tension lysimeters to simulate chemical reactions and transport processes. The hydraulic conductivity of the sediments determines soil moisture movement (Hogan et al., 2006), therefore it should be possible to employ this type of chemical monitoring at waterlogged sites as well. The challenge would be to relate archaeological materials to the rates of mineral loss and to work out how to convert SIs into percentage rates of loss (Crow, 2008). There are other significant factors such as water table fluctuations, wetting and drying and the presence or absence of bacteria and fungi which also need to be considered when predicting material degradation within the burial environment.
Fig. 4.3 SI indices showing the negative values at the terrestrial site. The actual percentage loss of mineral compared to the loss predicted by the Phreeqcii model, (solid line) actual loss and (broken line) predicted loss.

The results suggest that in the long term the mineral component of the antler samples would continue to deteriorate very slowly unless environmental conditions changed or unless the organic component of the material provided protection for the mineral against deterioration.

4.3.2. Fiskerton

The antler samples exhibited a degree of variation in the amount of deterioration between samples, particularly after 12 months and 18 months of burial. The greatest amount of deterioration occurred during the first few months of burial. After that there was little increase in the amount of deterioration. The antler samples retrieved after 12 months in fact had lower levels of deterioration than those retrieved after 18 months.

Horn samples showed an increase in the amount of deterioration over the whole period of burial. As with the antler samples the amount of deterioration was greater during the first six months of burial. After this, degradation continued throughout the whole burial...
period. The comparison of weight loss of antler and horn samples is shown in Fig. 4.4. There is less variation in the amount of deterioration in the horn samples than there is between the antler samples. Horn is formed from a single protein, keratin, unlike antler which is a more complex combination of protein collagen, and mineral, hydroxyapatite. The horn samples also contain no variation in physical structure between surfaces so this may cause the rate of deterioration to be more consistent. The horn samples would be subject to hydrolysis and after the process has begun it would continue unless conditions changed dramatically within the environment. The antler samples showed the highest levels of weight loss and also the greatest variation over the period of burial.

Fig. 4.4 Mean weight loss of horn and antler samples recovered after burial (antler, blue), (horn, red), illustrating the more regular pattern of weight loss of horn samples at the Fiskerton reburial site.
4.3.3. Firestone Copse

The percentage weight loss of antler, horn and ivory samples recovered from the burial site at Firestone Copse, station number 2 is shown in Figs.4.5 and 4.6. The samples used in the study were buried and recovered from a depth of 100 cm.

**Antler**

The antler samples showed the greatest total mean figure for weight loss over the period of the study with a high of 18.2%. They also showed the most variation in weight loss over each of the sample periods. The maximum weight loss again occurred during the first few months of burial.

![Graph](image)

**Fig. 4.5** Mean weight loss of horn and antler samples recovered after burial, (antler, blue), (horn, red), at the Firestone reburial site

The ivory samples showed slightly less weight loss than the antler samples with the highest mean recorded from the samples retrieved after 48 months of 15.2%. The variation in the weight loss of recovered samples was also less than that of the antler but marginally less than the mean weight loss of horn samples recovered after the same period of burial.
The initial weight loss after a short 3 months period of burial was highest with the ivory and antler samples. However the samples which were recovered after a longer period of burial indicated an equalization in the amount of deterioration occurring.

**Horn**

Fig.4.5 shows the weight loss of horn samples recovered from the Firestone site after 3, 12 and 48 months of burial, showing weight loss of three individual samples recovered at each time period and showing the mean weight loss of the same recovered samples. The pattern of weight loss with the horn samples does appear to be different than that of the other two materials. The first set of horn samples which were retrieved after 1 year had the lowest mean weight loss of 8.8 %. However the weight loss then increased in comparison to the other materials and after 48 months the mean loss was 15.2 % which was higher than antler.

**Ivory**

The weight loss of ivory samples recovered from Firestone after 3, 12 and 48 months of burial, showing weight loss of three individual samples recovered at each time period and, showing the mean weight loss of the same recovered samples is shown in Fig.4.6.

![Ivory weight loss](image)

**Fig. 4.6** Weight loss of ivory samples recovered from the Firestone site after 3 months, 12 months and 48 months of burial
4.3.4. Alum Bay

Weight loss of antler, horn and ivory samples recovered from Alum Bay after 3, 12 and 48 months of burial, showing the mean weight loss of the recovered samples is illustrated in Fig.4.7. The weight loss of antler samples becomes less as time passes.

![Weight loss of antler, horn and ivory samples recovered from Alum Bay site after 3 months, 12 months and 48 months of burial, showing the mean weight loss of the recovered samples](image)

**Fig. 4.7** Weight loss of antler, horn and ivory samples recovered from the Alum Bay site after 3 months, 12 months and 48 months of burial, showing the mean weight loss of the recovered samples

The maximum weight loss of the antler samples took place in the first 3 months after burial on the wreck site. The maximum mean weight loss of the samples was 19.5% recorded after the retrieval of samples after 3 months. The deterioration of the antler samples appears to be quite varied particularly the samples recovered after burial on the site for 3 months. The inconsistency shown here by this material is repeated at other burial sites. Fig.4.7 shows a less varied pattern of weight loss and the amount of weight...
loss reducing over the burial period. This clearly illustrates that the greatest degradation occurs initially over a short period of time.

Unlike the antler samples the maximum weight loss of ivory occurred in the samples recovered after 48 months. The increase in deterioration was small but still differed from the antler samples. The greatest mean weight loss recorded of the ivory samples was 16.2 % after 48 months.

There was a difference in the weight loss pattern of the horn samples at Alum Bay than those of the other two materials. The weight loss of the samples recovered after 3 months was 3.4 % less than that of the antler and 4.3 % less than ivory. The horn samples recovered after 48 months exhibited 25.2 % greater weight loss than the antler and 24.4 % greater weight loss than the ivory samples.

The horn samples interestingly showed a smaller weight loss than the other two materials after 3 months. The mean percentage weight loss increased steadily and after 48 months the horn samples had a greater weight loss than either the antler or the ivory samples.

4.3.5. Comparison of weight loss between the burial sites

The measurement of weight loss is a simple technique but very effective in highlighting the general extent of deterioration of samples without the use of sophisticated analytical techniques. It is however destructive and should not be used on sensitive archaeological materials. The mean weight loss of horn samples from the monitored sites and the period of burial can be seen in Table 4.1.
The greatest weight loss of the horn samples occurred in those buried at Alum Bay retrieved after 48 months of burial with a total weight loss of 40 % in comparison with a 15% weight loss of horn samples retrieved from Firestone after a similar period of burial. The next highest percentage weight loss occurred at Alice Holt where horn samples lost nearly 25 % of their original weight after 18 months of burial. The Firestone and Fiskerton sites showed similar levels of weight loss after 12 months both were less than Alum Bay and Alice Holt.

**Table 4.1** Mean weight loss of horn samples from each of the monitored sites and the length of their burial in months

<table>
<thead>
<tr>
<th>Site</th>
<th>% weight loss for different burial periods (months)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3</td>
</tr>
<tr>
<td>Alice Holt</td>
<td>18.6</td>
</tr>
<tr>
<td>Fiskerton</td>
<td>10.7</td>
</tr>
<tr>
<td>Firestone</td>
<td>8.8</td>
</tr>
<tr>
<td>Alum Bay</td>
<td>8.9</td>
</tr>
</tbody>
</table>

The weight loss of antler samples at each burial site is shown in Table 4.2. The greatest weight loss of the antler samples occurred in those buried at Alice Holt and retrieved after 18 months of burial with a total weight loss of 22.5 % in comparison with the next highest figure of 19.5 % weight loss of samples recovered from Firestone after 3 months of burial. The percentages of weight loss were highest in the first few months of burial. The weight loss continued to rise at Alum Bay and Alice Holt but fluctuated more at the Firestone and Fiskerton. This may be due to the composition of the material as the...
antler has a more dense outer layer and is less dense internally. The proportion of external to internal material in the sample may result in differential amounts of deterioration between samples. Alternatively there may be microenvironments within the sites which promote variations in the amount of deterioration. The weight loss of antler samples at Alum Bay was much less than that of horn at the same site.

Table 4.2 Mean weight loss of antler samples from each of the monitored sites and the length of their burial

<table>
<thead>
<tr>
<th>Site</th>
<th>% weight loss for different burial periods (months)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3</td>
</tr>
<tr>
<td>Alice Holt</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
</tr>
<tr>
<td>Fiskerton</td>
<td></td>
</tr>
<tr>
<td></td>
<td>16.6</td>
</tr>
<tr>
<td>Firestone</td>
<td></td>
</tr>
<tr>
<td></td>
<td>19.5</td>
</tr>
<tr>
<td>Alum Bay</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12.3</td>
</tr>
</tbody>
</table>

The results of the weight loss of the ivory samples at each retrieval period are shown in Table 4.3. No ivory samples were buried or recovered from Fiskerton or Alice Holt. At both burial sites the ivory samples continued to lose weight over the burial period. At each retrieval period the samples from Alum Bay showed slightly higher amounts of weight loss though they were less than the horn samples and more consistent than the antler samples. The samples deteriorated most during the first few months of burial and then less in the following period.
Table 4.3 Mean weight loss of ivory samples from each of the monitored sites and the length of their burial. Ivory samples were only buried and recovered from the Firestone and Alum Bay burial sites

<table>
<thead>
<tr>
<th>Site</th>
<th>% weight loss for different burial periods (months)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3</td>
</tr>
<tr>
<td>Firestone</td>
<td>12.7</td>
</tr>
<tr>
<td>Alum Bay</td>
<td>13.2</td>
</tr>
</tbody>
</table>

The deterioration of horn is highest at Alum Bay and next highest at Alice Holt. The deterioration is similar at Firestone and Fiskerton. This fits the expected pattern. The greatest deterioration in antler samples took place at Alice Holt with the lowest deterioration at Firestone although initial rates of degradation were high at this site. Ivory samples deteriorated slightly more rapidly at Alum Bay than they did at Firestone. Horn appears most vulnerable at Alum Bay this supports the predictive table in Chapter 1 (Watkinson, 1987). The sites each ranked by amount of weight loss after a burial period of 12 months are shown in Table 4.4. Alice Holt and then Alum Bay appear to cause the highest weight loss with Fiskerton causing the least amount of weight loss for horn samples. The table shows that the horn samples incurred the greatest weight loss at Alum Bay as did the ivory samples. Fiskerton showed the lowest weight loss of samples. Firestone had the next lowest amount of weight loss so both waterlogged reduced sites had lower weight losses than Alice Holt and the aerobic marine environment at Alum Bay. The measurement of weight loss is a relatively simple technique to carry out but by being inclusive it incorporate changes which have been caused by, chemical, physical and biological means.
Table 4.4 Sites ranked 1-4 by weight loss; 1 highest, 4 lowest after 12 months burial

<table>
<thead>
<tr>
<th>Site</th>
<th>Horn Weight loss%</th>
<th>Antler Weight loss%</th>
<th>Ivory Weight loss%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alice Holt</td>
<td>2</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Fiskerton</td>
<td>4</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>Firestone</td>
<td>3</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Alum Bay</td>
<td>1</td>
<td>3</td>
<td>1</td>
</tr>
</tbody>
</table>
4.4. SEM and EDAX Analysis

SEM and EDAX analysis were undertaken in order to examine physical deterioration and to observe whether microorganisms were present on the surface of recovered samples. EDAX analysis was used in conjunction with the SEM to record any changes in elemental composition which may have occurred.

The unburied horn sample at lower magnification (x550), illustrates its plate-like structure. At higher magnification (x5000), fragments and debris can be seen on the surface. The antler sample is much more fibrous under the microscope and, at higher magnification, surface lacunae are visible. The ivory sample appears to be smoother and more coherent but at the higher level of magnification many small cracks can be seen on the surface. The striations visible on the sample surfaces were caused during preparation when a hacksaw was used to cut the samples. SEM images and EDAX analysis results for unburied horn, antler and ivory samples are illustrated by Figs.4.8 and 4.9.

The antler and ivory samples show their similarity in composition in the EDAX analysis. They both exhibit large peaks for calcium and phosphorus which are the major elements of hydroxyapatite which is the mineral component of both antler and ivory, although there are slight differences in the composition of mineral between the two materials. Antler consists primarily of carbonatehydroxylapatite, \([\text{Ca}_{10}(\text{PO}_4)_3(\text{CO}_3)_3(\text{OH})_2]\) and calcium phosphate carbonate \([\text{Ca}_{10}(\text{PO}_4)_6\text{CO}_3]\) whilst ivory is predominantly carbonatehydroxylapatite \([\text{Ca}_{10}(\text{PO}_4)_3(\text{CO}_3)_3(\text{OH})_2]\).

Horn has a large sulfur peak which is indicative of the large number of disulfide bonds which occur in the protein keratin, the major constituent of horn.
Fig. 4.8 SEM images of unburied horn, antler and ivory, no bacteria visible
Fig. 4.9 EDAX analysis of unburied antler, horn, and ivory
4.4.1. Alice Holt

Antler samples exposed and recovered from the leaf litter are illustrated in Fig. 4.10. Both samples are physically weathered and have weathering products on the surface. They also have cracks on the surface. The sample from the leaf litter appears to have slightly more surface debris than the exposed sample, Fig. 4.10, (c) and (d).

Fig. 4.10 Antler samples recovered after 6 months exposed at Alice Holt
No samples were recovered either exposed or from the leaf litter after 20 months. The antler sample recovered from H1 did not show much surface debris or cracking, however, it was weathered and contained bacteria on the surface. The sample from H2 was more weathered and bacteria were clearly visible on the surface. This pattern was repeated in the sample from H3 which had more extensive surface weathering and bacteria clearly visible on the surface.

EDAX analyses of the antler samples recovered after a 20 month burial period (Fig. 4.12) show differences between those carried out on the 6 month samples. Samples from all three burial horizons H1, H2 and H3 showed a similar pattern of large calcium and phosphorus peaks as in the 6 month samples. However the 20 month samples had small carbon peaks, this could indicate that bacteria are beginning to breakdown the samples.
(a) Antler x 1000 Horizon 1
(b) Antler x 5000 Horizon 1
(c) Antler x 5000 Horizon 2
(d) Antler x 5000 Horizon 2
(e) Antler x 1000 Horizon 3
(f) Antler x 5000 Horizon 3

Fig. 4.11 Antler samples recovered after 20 months burial at Alice Holt, Burial Horizon 1, showing bacteria on surface, (arrowed)
Fig. 4.12 EDAX analysis of antler samples recovered after 20 months burial in Burial Horizon 1
The exposed horn sample is very weathered with lots of surface debris and is beginning to split and delaminate. The sample from the leaf litter has some surface debris and is beginning to delaminate but not as badly as the exposed sample shown in Fig. 4.13.

(a) Horn x 1000 exposed  
(b) Horn x 5000 exposed

(c) Horn x 1000 leaf litter  
(d) Horn x 5000 leaf litter

**Fig. 4.13** Horn samples recovered after 6 months burial at Alice Holt, exposed and leaf litter sample
The EDAX analyses of the two samples which were exposed and buried in the leaf litter illustrated in Fig.4.14, show strong sulfur peaks from the disulphide bonds which are a major proportion of the structure of keratin. The sample from the leaf litter also shows high peaks of aluminium and silicon, which are possibly clay minerals from the burial environment.

(a) Horn exposed

(b) Horn leaf litter

**Fig. 4.14** EDAX spectra of horn samples recovered from the leaf litter and exposed for 6 months at Alice Holt
The sample from Burial Horizon 1 recovered after 20 months burial is shown in Fig.4.15, it appeared to have a greater level of physical weathering and delamination including large cracks and fissures. Bacteria can also be clearly observed within the fissures. The sample from Burial Horizon 2 is also highly weathered with debris and bacteria visible on the surface. The surface of the sample recovered from Burial Horizon 3 has less visible debris and weathering but a large number of bacteria are visible on the surface. Generally the SEM images appear to show a considerable increase in physical deterioration of the samples which were recovered after 20 months burial than those recovered after 6 months. The increased number of bacteria evident on the 20 month sample can clearly be seen, Fig.4.15, (a) and (f).

After 20 months the samples showed sulfur peaks with aluminium and silica. After burial for 6 months the horn samples recovered from Alice Holt, both SEM and EDAX charts, showed no evidence of bacterial activity. However the samples recovered after 20 months show bacteria clearly visible on the surface. The EDAX charts also illustrate surface differences between the horn samples recovered after 6 months and 20 months. Similarly the occurrence of iron on the surfaces of the samples is shown by EDAX spectra.
Fig. 4.15 Horn samples recovered after burial for 20 months at Alice Holt.
4.4.2. Fiskerton

The SEM image of the antler sample recovered after 6 months illustrated by Fig. 4.16 (b), shows that the sample is already very weathered with debris on the surface and some cracking. Small numbers of bacteria are also visible on the surface. After 12 months burial the sample surface is extremely weathered with substantial cracking and visible bacteria. The same pattern is evident on the 18 month sample which shows substantial weathering extensive cracking and bacteria on the surface see Fig. 4.16, (d).

EDAX analysis of the antler samples recovered from Fiskerton is illustrated in Fig. 4.17. After 12 months there is a noticeable iron peak. After 18 months burial the analysis showed proportionally smaller calcium and phosphorus peaks with a much larger iron peak. There was a steady increase in the amount of iron and increasing numbers of bacteria for each burial period suggesting an increase in the amount of deterioration with lengthening time of burial.
Fig. 4.16 SEM Antler samples recovered from Fiskerton after burial for 6 months. Bacteria are also visible.
Fig. 4.17 EDAX analysis of antler samples recovered after 12 months, and 18 months from Fiskerton. The proportionate increase in iron becomes obvious as the burial period lengthens.
The SEM images of the horn sample recovered after burial for 6 months are shown in Fig.4.18. Physical weathering can be seen on the surface. There are also a number of cracks and small numbers of bacteria present on the sample see Fig.4.18, (b). On the sample recovered after 18 months burial the surface is very broken up physically.

(a) Horn x 1000, 6 months
(b) Horn x 5000, 6 months
(c) Horn x 1000, 18 months
(d) Horn x 5000, 18 months

Fig. 4.18 SEM horn samples recovered from Fiskerton after 6 months
EDAX analysis of the horn sample recovered after burial for 12 months is illustrated in Fig. 4.19. The EDAX analysis of the horn sample showed an intense peak for iron. The iron showed as a much smaller proportion on the 18 month sample though it was still present. The reasons for this are unclear but may possibly be related to changes in the water table.

![Horn 12 months](image.png)

**Fig. 4.19** EDAX analysis of horn sample recovered from Fiskerton after 12 months

### 4.4.3. Firestone Copse

SEM and EDAX analyses were undertaken on horn, ivory and antler samples buried and recovered from the brackish wetland burial site located within the Firestone 2 monitoring station after 48 months of burial.

The ivory sample recovered after 48 months which can be seen in Fig. 4.20, shows extensive deterioration with surface weathering, cracking and delamination. There are no bacteria visible on the SEM images from this site.
Fig. 4.20 SEM images of ivory samples recovered after 48 months burial at Firestone

Fig. 4.21, shows the EDAX results for ivory samples recovered after burial for 48 months at the Firestone 2 monitoring station. The graph shows peaks for calcium and phosphorus, the major mineral constituents of the material. There is also a small iron peak.

Fig. 4.21 EDAX charts of an ivory sample recovered after burial for 48 months at Firestone
The SEM image of the antler sample recovered after burial for 48 months burial at Firestone is illustrated in Fig. 4.22. It showed extensive weathering with large cracks and surface debris. There are no obvious signs of bacteria on the samples surface.

![Antler x 1000, 48 months](image1)

![Antler x 5000, 48 months](image2)

**Fig. 4.22** SEM images of Antler samples recovered 48 months of burial at Firestone

The EDAX results for the buried antler sample recovered after 48 months is illustrated in Fig. 4.23. The chart shows peaks for calcium and phosphorus corresponding to hydroxyapatite, the mineral component of the antler and is similar to the charts of ivory samples recovered from this site. There is also a small amount of iron present.

![Antler, 48 months](image3)

**Fig. 4.23** EDAX charts of antler sample recovered from Firestone after burial for 48 months at Firestone
After 48 months burial the horn sample shows extensive surface deterioration and delamination, with debris on the surface, lacunae and fibre disintegration, this is shown in Fig.4.24.

![Horn x 1000, 48 months](image1)
![Horn x 5000, 48 months](image2)

**Fig. 4.24** SEM images of horn samples recovered from Firestone after 48 months showing very extensive weathering, cracking and debris on surface, lacunae and fibres coming apart

The EDAX results for horn samples, buried and recovered after 12 and 48 months are illustrated in Fig 4.25. Both samples have peaks representing iron on their surfaces. The intensity of this peak is proportionally greater on the sample recovered after 12 months than it is on the sample recovered after 48 months
4.4.4. Alum Bay

SEM images of ivory samples recovered from Alum Bay are shown in Fig. 4.26. After only 3 months of burial, extensive cracking and weathering was visible on the surface of the sample and also the microscopic remains of diatoms can be seen, see Fig. 4.26,
(b) highlighted with an arrow and bacteria visible on the surface of image (d) are also highlighted with an arrow.

The ivory sample recovered after 12 months burial at the marine site exhibited weathering and surface debris and extensive cracking. The prismatic structure of the material is visible in the cracks there is a large amount of debris on the surface including weathering products.

![SEM images of ivory samples recovered from Alum Bay after 3 months](image)

(a) Ivory x 1000, 3 months  (b) Ivory x 5000, 3 months

(c) Ivory x 1000, 12 months  (d) Ivory x 5000, 12 months

**Fig. 4.26** SEM images of ivory samples recovered from Alum Bay after 3 months

EDAX charts of ivory samples recovered from Alum Bay are illustrated below in Fig. 4.27, the charts of the recovered samples from burial periods 12 months and 48 months, are very similar with peaks for calcium and phosphorus corresponding to the
hydroxyapatite mineral fraction within the ivory samples. All of the samples have a small amount of iron on the surface. The intensity of the iron peak appears to increase with the increasing length of burial time. Small amounts of sodium and chloride on the surface are indicative of the marine environment.

Fig. 4.27 EDAX spectra of ivory samples recovered from Alum Bay after 12 months and 48 months

SEM images of antler samples recovered after 12 months and 48 months of burial at Alum Bay are illustrated in Fig.4.28. After burial for 12 months, the samples exhibited extensive weathering with severe surface deterioration. After 48 months the sample had cracks, surface deterioration and weathering, with remains of marine diatoms also

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visible. Samples recovered after 48 months exhibited very extensive weathering and debris on the surface with many remains of marine diatoms on the surface, Fig. 4.28, (c) and (d), arrowed.

![SEM images of antler samples from Alum Bay recovered after 12 months and 48 months of burial](image)

Fig. 4.28 SEM images of antler samples from Alum Bay recovered after 12 months and 48 months of burial

EDAX charts of antler samples recovered after 12 months and samples recovered after 48 months are illustrated in Fig. 4.29. The graphs are very similar showing peaks for calcium and phosphorus corresponding to the hydroxyapatite mineral fraction of the antler there are also clay minerals present from the environment on all three samples with oxygen and a small amount of iron. There are also small amounts of sodium and chloride on the surface which are indicative of the marine environment.
Fig. 4.29 EDAX spectra of antler samples recovered after 12 months and antler samples recovered after 48 months of burial at Alum Bay.

SEM images of horn samples are shown in Fig. 4.30. The sample recovered after burial for 3 months at Alum Bay shows extensive deterioration of the surface and a breakdown of the fibre structure. Samples recovered after 48 months exhibited very extensive weathering with cracking and debris on surface. Lacunae were also visible on the surface and the erosion effect visible on image (d), arrowed, appears to show degradation caused by the activity of bacteria. After 3 months the surface appears to be delaminating but after 48 months the whole of the surface appears to be eroding.
EDAX charts of horn samples recovered after 3 months and 48 months of burial at Alum Bay are illustrated in Fig.4.31. The graphs are quite similar in the major constituents showing peaks for sulfur corresponding to the disulfide bonds within the keratin molecules. There are small amounts of sodium and chloride indicative of the marine environment.
Fig. 4.31 EDAX spectra of horn samples recovered from Alum Bay after burial for 3 months, and horn samples recovered after burial for 48 months.

4.4.5 Evaluation of SEM and EDAX data

SEM images of an unburied horn sample and horn samples recovered from the various burial sites are shown below in Fig 4.32. The unburied sample shows its plate like structure whilst the in the sample recovered after burial at Alice Holt for 20 months both delamination and bacteria are clearly visible. The Fiskerton sample is delaminated and the sample recovered from Firestone shows clearly that fibres are coming apart, whilst the sample from Alum Bay shows extensive degradation caused by microorganisms.
**Horn**

**Fig. 4.32** Unburied horn sample and horn samples recovered from the burial sites

SEM images of an unburied antler sample and antler samples recovered from the various burial sites are shown below in Fig 4.33
Antler

Fig. 4.33 Unburied antler sample and antler samples recovered from the burial sites
The unburied sample shows its fibrous nature and lacunae which would have been occupied by blood vessels during the life of the animal. The sample recovered from Alice Holt shows the surface beginning to break down but no extensive degradation. The surfaces of samples from the other burial sites show deterioration of the surface with debris which on the sample from Alum Bay includes pieces of shell from marine crustaceans or molluscs.

**Ivory**

SEM images of ivory samples recovered from Firestone and Alum Bay are illustrated in Fig. 4.34.

Ivory Unburied

Ivory Firestone 48 months

Ivory Alum Bay 12 months

**Fig. 4.34** Unburied ivory sample and ivory samples recovered from the burial sites
The unburied ivory sample shows a smooth surface though there are numerous minute cracks evident on the surface. The sample recovered from Firestone shows physical deterioration of the surface whilst the sample recovered from Alum Bay has large cracks and fissures showing extensive physical deterioration.

In an effort to summarise the physical and biological changes observed on the samples by SEM analysis, a number of damage indicators were described for each type of sample material. These indicators were numbered and tabulated and then attributed to control samples before comparing them with buried and retrieved samples. The data is useful in describing the type of physical change in the appearance of samples which occurs between burial periods. The damage indicators determined on after observation of the samples are described below. Most of the indicators are applicable to all of the materials, but an indicator such as delamination is appropriate for horn samples, but is not applicable to antler samples. The results are qualitative but are an attempt to introduce concepts of change through time into the degradation processes. The damage indicators identified are set out below:

1. **Fibres beginning to part.** The fibre structure of the material begins to become less coherent, with gaps becoming visible in the structure

2. **Surface lacunae.** Pits and cavities appear on the surface of the sample

3. **Bacteria visible on the surface.** No bacteria were visible on the surfaces of the control samples. However bacteria could be clearly observed on a number of the retrieved samples.

4. **Surface weathering.** This was used as a description of visible disruption on the surface of a sample.
5. **Debris on surface.** Weathering products from the surface of the sample and material from the surrounding burial environment appear on the surface.

6. **Delamination.** Horn is a material which can delaminate. Its layered structure facilitates this form of deterioration.

7. **Surface cracks.** Development of substantial cracks on the surfaces of the samples

Samples with visible bacteria on SEM images included:

- Alice Holt, antler sample recovered after 20 months, horn sample recovered after 20 months.
- Fiskerton, antler 6 months, 12 months and 18 months and horn 6 months and 18 months.
- Alum Bay, ivory samples recovered after 4 years, horn samples recovered after 12 months and 48 months.

The damage indicators observed on recovered ivory samples are shown in Table 4.5.

Ivory samples were only buried and recovered from Firestone and Alum Bay. After a burial period of 3 months at Firestone exhibited 3 damage indicators which increased to 4, after burial periods of 12 and 48 months. Pits and lacunae began to develop on the surface of the recovered samples after a 12 month burial period. At Alum Bay 5 damage indicators were visible after a 3 month burial period and this number remained the same throughout the whole burial period.
### Table 4.5: Damage indicators observed on samples recovered from the reburial sites

<table>
<thead>
<tr>
<th>Material</th>
<th>Damage indicator</th>
<th>Occurrence of damage indicators after different burial periods at each site</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Alice Holt</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5 6 12 18 48</td>
</tr>
<tr>
<td>Ivory</td>
<td>Fibres begin to part</td>
<td>+ + + + +</td>
</tr>
<tr>
<td></td>
<td>Surface Lacunae</td>
<td>+ + + + +</td>
</tr>
<tr>
<td></td>
<td>Bacteria visible</td>
<td>+ + + + +</td>
</tr>
<tr>
<td></td>
<td>Surface weathered</td>
<td>+ + + + +</td>
</tr>
<tr>
<td></td>
<td>Surface debris</td>
<td>+ + + + +</td>
</tr>
<tr>
<td></td>
<td>Delaminated</td>
<td>+ + + + +</td>
</tr>
<tr>
<td></td>
<td>Surface cracks</td>
<td>+ + + + +</td>
</tr>
<tr>
<td>Horn</td>
<td>Fibres begin to part</td>
<td>+ + + + +</td>
</tr>
<tr>
<td></td>
<td>Surface Lacunae</td>
<td>+ + + + +</td>
</tr>
<tr>
<td></td>
<td>Bacteria visible</td>
<td>+ + + + +</td>
</tr>
<tr>
<td></td>
<td>Surface weathered</td>
<td>+ + + + +</td>
</tr>
<tr>
<td></td>
<td>Surface debris</td>
<td>+ + + + +</td>
</tr>
<tr>
<td></td>
<td>Delaminated</td>
<td>+ + + + +</td>
</tr>
<tr>
<td></td>
<td>Surface cracks</td>
<td>+ + + + +</td>
</tr>
<tr>
<td>Antler</td>
<td>Fibres begin to part</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Surface Lacunae</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>Bacteria visible</td>
<td>+ + + + +</td>
</tr>
<tr>
<td></td>
<td>Surface weathered</td>
<td>+ + + + +</td>
</tr>
<tr>
<td></td>
<td>Surface debris</td>
<td>+ + + + +</td>
</tr>
<tr>
<td></td>
<td>Delaminated</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Surface cracks</td>
<td>+ + + + +</td>
</tr>
</tbody>
</table>
A horn sample recovered after burial at Alice Holt for a period of 6 months had only 1 visible damage indicator. A sample examined after burial for 12 months at the same site had 5 damage indicators indicating a large increase in deterioration over this period. The brackish wetland and the freshwater wetland had a similar pattern with damage indicators visible after a short period of burial and then did not change in later periods. Samples from Alum Bay had a high number of damage indicators after a short period of burial then a lower number in later periods. The indicators which were present in the later retrieval periods were numbers, 3, bacteria visible on the surface, 4, surface weathering and 5, debris on the surface.

Ivory samples generally showed less observable damage at Firestone than at Alum Bay and the observed damage on ivory samples occurring more rapidly and extensively at Alum Bay. Antler appeared to deteriorate slowly at Alice Holt with only a slow increase in observed degradation over time. At Fiskerton the deterioration began slowly but was ultimately greater than at Alice Holt. At Firestone deterioration was generally slow but greater initially at Alum Bay which became less obvious over a longer time period. Horn samples appeared to deteriorate slowly initially at Alice Holt but much more rapidly as time passed. This is interesting in proving that appearances can be deceptive. At Fiskerton the trend appeared to be that the horn samples deteriorated quickly initially but then appeared to stabilise in time. At the Firestone burial site the horn samples appeared to deteriorate rapidly at first and then to slow down. In all other tests carried out it was obvious that the horn samples were more highly degraded than the other materials particularly at the Alum Bay burial site.

Most frequently, the damage indicators increase in number with the length of time in which the samples have been buried. The horn samples had a high number of damage
indicators recorded at all of the burial sites, a total of 4 at Fiskerton and 5 at the other
sites. Antler had a highest recorded number of 5 damage indicators at Fiskerton and also
at Firestone, with a highest recorded figure of 4 at Alice Holt and Alum Bay. Ivory had
a highest recorded figure of 5 at Alum Bay and 4 at Firestone. The number of damage
indicators is high indicating that a large amount of physical deterioration was observed
on the retrieved samples in comparison with unburied samples.

The most significant elemental changes recorded by EDAX analysis are changes in
levels of both iron and sulfur on the surface of various samples. These elements were
not present on the surface of any of the control samples but occur on some of the
recovered samples. Iron may play a role in the breakdown of the material by releasing
sulfur and by bonding with the hydroxyapatite in the antler and ivory. Sulfur was not
included in the analysis of the horn samples because it is a significant part of the natural
structure of keratin, although it would be released as the keratin is subject to hydrolysis
particularly in alkaline conditions.

Samples with iron peaks on EDAX spectra were recorded and the sites where they
occurred were noted. The EDAX charts of unburied horn, antler and ivory are shown
below in Fig.4.35 for comparative purposes. The similarities between ivory and antler
samples are obvious as is the dissimilarity of the unburied horn sample. The surface of
antler and ivory comprises mainly calcium, phosphorus and oxygen whilst horn consists
mainly of sulfur and oxygen.
Horn Unburied

Antler Unburied

Ivory Unburied

Fig. 4.35 EDAX charts of unburied horn, antler and ivory samples
The differences in elemental composition between the unburied samples and a number of recorded samples from various burial sites are described below.

**Fiskerton.** An antler sample with iron and a small trace of sulfur from samples recovered after 18 months and a horn sample recovered after 12 months showing a peak for iron are shown below in Fig 4.36

![EDAX chart of a horn sample recovered after 12 months](image1)

Fiskerton Horn 12 months

![EDAX chart of an antler sample recovered after 18 months](image2)

Fiskerton Antler 18 months

**Fig. 4.36** EDAX charts of a horn sample recovered after 12 months and an antler sample recovered after 18 months from Fiskerton
**Firestone.** An antler sample recovered after 12 months with a peak of iron and a horn sample recovered after 12 months showing an iron and sulfur peak are shown below in Fig.4.37.

![EDAX charts of a horn sample and an antler sample](image)

**Fig. 4.37** EDAX charts of a horn sample recovered after 12 months and an antler sample recovered after 12 months from Firestone
**Alum Bay.** Ivory samples recovered after 48 months showed iron and sulfur peaks. The horn sample recovered after 3 months has an iron peak. These charts are illustrated below in Fig.4.38.

Interestingly the peaks for iron which appear on the buried samples were not visible on the unburied samples therefore they were probably derived from the burial
environments. The peaks appear on samples from three of the burial sites but not on samples from Alice Holt. It would appear that the waterlogged sites are sites which are producing iron on the surface of buried samples. Samples showing sulfur and iron peaks on the EDAX spectra included an antler sample from Fiskerton recovered after 18 months. A horn sample recovered after 18 months also exhibited a peak for iron. At Firestone an antler sample recovered after 12 months and horn samples recovered after 3 months, 12 months and 48 months showed peaks for iron. At Alum Bay an ivory sample recovered after 4 years and a horn sample recovered after 3 months had peaks for iron. Sulfur was not included in the analysis of the horn samples because it is a significant part of the natural structure of keratin. Iron may play a role in the breakdown of the material by breaking bonds within the chains of amino acids releasing sulfur and by bonding with hydroxyapatite in the antler and ivory.

4.5. Fourier Transform Infra Red Spectroscopy, (FTIR) analysis

FTIR analysis is used in the analysis of organic materials to determine the extent of degradation and also to identify them. It has been used to determine the deterioration of collagen in bone (Chadefaux et al., 2008) and used in the identification of keratin based materials such as tortoiseshell. Therefore it was felt that it would be a useful technique to examine the amount of degradation which had occurred in the horn, antler and ivory samples recovered from the burial sites. Deterioration was looked for in spectra from protein bands and from peaks relating to the mineral component of the antler and ivory samples. In this study simple ratios were calculated between the two protein bands and between the protein band and the mineral peak. In reality each protein band consists of a number of peaks relating to different types of bonds within the secondary structure of the protein molecules. The examination of peak intensity within the bands themselves
would give a greater insight into the amount and type of degradation taking place within the samples. However the data produced is interesting and the protein mineral ratios are particularly relevant. The protein bands used in the study were measured at wavenumber 1640 cm\(^{-1}\) and 1540 cm\(^{-1}\) for horn, antler and ivory samples. The protein bands referred to at wavenumber 1640 cm\(^{-1}\) are referred to as PI in the text and the protein bands measured at wavenumber 1540 cm\(^{-1}\) are referred to as PII.

The samples used in the analysis of FTIR spectra were recovered after burial for the same period as those used above in the combined SEM and EDAX images and charts, except the spectra of the Alum Bay sample which was the spectra of the sample buried for 48 months. This was selected because it was radically different in shape from the others. The peak observed at wavenumber 1020 cm\(^{-1}\) on antler and ivory samples is diagnostic of hydroxyapatite the mineral component of the materials. This was used in conjunction with the PII bands to calculate a ratio between the materials to establish if there were changes taking place between the protein and mineral components of the materials at the reburial sites. The composition of ivory is similar to antler and bone and so the measurement of ivory spectra was carried out using the same wavenumbers as the antler samples. The PI peak for horn was measured at a wavenumber of 1640 cm\(^{-1}\) whilst the PII peak was measured at a wavenumber of 1540 cm\(^{-1}\). The ratio of PII to PI protein bands in unburied samples of horn antler and ivory are shown in Table 4.8.

The ratio of PII to mineral is also shown for the unburied antler and ivory samples. Samples of 125,000 year old mammoth tusk and bison horn are also illustrated for comparative purposes. There are differences between the spectra of bison and horn control and mammoth and ivory control when compared with buried samples. The ratio of PII to PI in the horn control sample was 0.76. In the sample taken from bison horn the figure was 0.64, a decrease of 12%. This suggests that protein is degrading but even
in the samples of mammoth ivory protein can still be detected even though the proportions are less than in modern ivory samples. The ratio in the unburied horn sample would be indicative of the ratio of proteins within keratin whilst the bison would be indicative of the protein ratios within the bone core of the bison horn. The ratio of PII protein bands to hydroxyapatite is greatest in antler and considerably less in mammoth ivory indicating that over time protein has degraded proportionally in respect of the hydroxyapatite. The changes are generally indicative of a breakdown of proteins, collagen in the cases of antler and ivory and keratin in the case of horn.

**Table 4.6** The Ratio of PII to PI bands and PII to hydroxyapatite of control samples compared with samples recovered from the reburial sites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wavenumber and peak intensity above baseline</th>
<th>Ratio%</th>
<th>Ratio%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1640</td>
<td>1540</td>
<td>1020</td>
</tr>
<tr>
<td>Antler</td>
<td>0.40</td>
<td>0.27</td>
<td>0.99</td>
</tr>
<tr>
<td>Ivory</td>
<td>0.46</td>
<td>0.27</td>
<td>0.99</td>
</tr>
<tr>
<td>Mammoth</td>
<td>0.10</td>
<td>0.11</td>
<td>0.99</td>
</tr>
<tr>
<td>Horn</td>
<td>0.98</td>
<td>0.74</td>
<td></td>
</tr>
<tr>
<td>Bison</td>
<td>0.15</td>
<td>0.10</td>
<td></td>
</tr>
</tbody>
</table>

The FTIR spectra of horn samples from Alum Bay showed a clear change after a long burial period. Around wavenumber 830 cm\(^{-1}\) there is a new peak that does not appear on control samples of this material. In this case the peak is liable to be caused by loose sediment physically trapped in the surface of the deteriorated sample. A peak at around this wavenumber is also evident on a bison sample from Newtown dating to around 125 thousand years ago. In this case the peak is likely to be caused by the mineral proportion of the horn core. The keratin would have degraded leaving the core behind.
4.5.1. Horn

The combined FTIR spectra of horn samples from each of the burial sites and a control sample are illustrated in Fig. 4.39. There are differences between the samples in the intensities of the protein peaks. This is particularly obvious when looking at the spectra from the marine site. This spectrum has less intense peaks but has a large peak around the 840 cm\(^{-1}\) wavenumber. Complete mineralisation leading to fossilisation is a very slow process (Shelton and Johnson, 1995), therefore it would be likely that this mineral is derived from the surrounding burial environment but loosely adhering to the material without being chemically bonded and integrated into the substrate.

A similar peak is also present on the sample taken from bison horn which also came from a marine context. In this case the outer sheath of keratin has probably degraded leaving the bone core to be preserved. The ratios are shown in Table 4.9.

![Combined FTIR spectra of horn samples from each of the burial sites and an unburied sample](image)

**Fig. 4.39** Combined FTIR spectra of horn samples from each of the burial sites and an unburied sample Key: black; unburied, green; Alice Holt, green; Fiskerton, purple; Firestone, blue; Alum Bay
At Alice Holt the ratios of P II to PI bands in the horn samples did vary according to the period of burial. The relative protein peak heights of horn samples are shown in Table 4.7. Those buried for a longer period exhibited a lower percentage of PII to PI bands suggesting that the change in the ratio is due to deterioration of the PI in relation to PII bands. The variations in ratios for the horn samples from Fiskerton are very similar to those from Alice Holt. The percentage increases over the burial period but the levels are quite similar between sites. The changes were small Fiskerton where the ratio of P II to PI fell slightly over the burial period. The biggest change occurred at Alum Bay which appeared to cause more protein degradation as predicted (Watkinson, 1987). The rate of change is slow at Firestone which is the most neutral of the sites. The Fiskerton site was classed as slightly acidic and could be considered to be more protective of protein than the other sites.
Table 4.7 Relative peak heights above a baseline of horn samples at specific wavenumbers

<table>
<thead>
<tr>
<th>Site</th>
<th>Material/Horn</th>
<th>Wavenumber cm⁻¹</th>
<th>Ratio%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Firestone</td>
<td>Period (months)</td>
<td>1640</td>
<td>1540</td>
</tr>
<tr>
<td>3</td>
<td>0.99</td>
<td>0.85</td>
<td>0.85</td>
</tr>
<tr>
<td>12</td>
<td>0.99</td>
<td>0.89</td>
<td>0.89</td>
</tr>
<tr>
<td>48</td>
<td>0.99</td>
<td>0.90</td>
<td>0.90</td>
</tr>
<tr>
<td>Alum Bay</td>
<td>Period (months)</td>
<td>1640</td>
<td>1540</td>
</tr>
<tr>
<td>3</td>
<td>0.99</td>
<td>0.83</td>
<td>0.84</td>
</tr>
<tr>
<td>12</td>
<td>0.46</td>
<td>0.46</td>
<td>1.00</td>
</tr>
<tr>
<td>48</td>
<td>0.32</td>
<td>0.35</td>
<td>1.10</td>
</tr>
<tr>
<td>Fiskerton</td>
<td>Period (months)</td>
<td>1640</td>
<td>1540</td>
</tr>
<tr>
<td>6</td>
<td>0.99</td>
<td>0.90</td>
<td>0.90</td>
</tr>
<tr>
<td>12</td>
<td>0.99</td>
<td>0.86</td>
<td>0.87</td>
</tr>
<tr>
<td>18</td>
<td>0.99</td>
<td>0.86</td>
<td>0.86</td>
</tr>
<tr>
<td>Alice Holt</td>
<td>Burial horizon/period (months)</td>
<td>1640</td>
<td>1540</td>
</tr>
<tr>
<td>H1 6</td>
<td>0.99</td>
<td>0.81</td>
<td>0.82</td>
</tr>
<tr>
<td>H2 6</td>
<td>0.99</td>
<td>0.85</td>
<td>0.86</td>
</tr>
<tr>
<td>H3 6</td>
<td>0.99</td>
<td>0.85</td>
<td>0.86</td>
</tr>
<tr>
<td>H1 20</td>
<td>0.99</td>
<td>0.90</td>
<td>0.90</td>
</tr>
<tr>
<td>H2 20</td>
<td>0.99</td>
<td>0.90</td>
<td>0.91</td>
</tr>
<tr>
<td>H3 20</td>
<td>0.99</td>
<td>0.89</td>
<td>0.89</td>
</tr>
</tbody>
</table>

In unburied horn samples the ratio of PII to PI protein bands was 0.76. The deterioration of the same proteins in samples from Firestone increased to 0.85 after 3 months and to 0.90 after 48 months 14% higher than the unburied samples. At Fiskerton the ratios were 0.90 after 6 months but then slowed and were only 0.86 after 18 months an increase in deterioration of 10% from the unburied sample but much less change over time. At Alice Holt the ratios were 10% greater than in unburied horn samples increasing after 20 months burial to a maximum of 15% increase in deterioration at Horizon 2. The deterioration in the ratio of proteins occurred in the samples recovered after 14 months at Alum Bay. Here the ratio after 48 months was 1.10 an increase of 36% compared with the unburied samples.
4.5.2. Antler

The combined spectra of antler samples and an unburied antler sample are shown in Fig. 4.40. The combined spectra show the differences between the samples from different burial environments. The spectra highlight the relative differences in the height of the protein peaks in samples recovered from differing environments.

![FTIR spectra of antler samples](image)

**Fig. 4.40** Combined FTIR spectra of antler samples from each of the burial sites and a control sample. Key: black; control, red; Alice Holt, green; Fiskerton, purple; Firestone, blue; Alum Bay.

The ratio of PII to P I was higher in the buried and retrieved samples suggesting that deterioration was taking place. The biggest difference occurred at Alum Bay after a burial period of 48 months, where the ratio increased to 1.09, the ratio increased slowly at Firestone and decreased at both Alice Holt and Fiskerton. Fiskerton was considered to have the most protective environment for the preservation of horn, whilst the Alice Holt may have less hydrolysis as it is not permanently waterlogged. Results of FTIR
analyses of antler samples recovered from all of the burial sites are shown below in Table 4.8.

**Table 4.8** Relative peak heights above a baseline of antler samples at specific wavenumbers

<table>
<thead>
<tr>
<th>Site</th>
<th>Material/Antler</th>
<th>Wavenumber cm(^{-1})</th>
<th>Ratio %</th>
<th>Ratio%</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alice Holt</strong></td>
<td><strong>Burial period (months)</strong></td>
<td>1640</td>
<td>1540</td>
<td>1020</td>
</tr>
<tr>
<td>H1 6</td>
<td></td>
<td>0.48</td>
<td>0.33</td>
<td>0.91</td>
</tr>
<tr>
<td>H2 6</td>
<td></td>
<td>0.39</td>
<td>0.26</td>
<td>0.97</td>
</tr>
<tr>
<td>H3 6</td>
<td></td>
<td>0.43</td>
<td>0.30</td>
<td>1</td>
</tr>
<tr>
<td>H1 20</td>
<td></td>
<td>0.59</td>
<td>0.40</td>
<td>0.99</td>
</tr>
<tr>
<td>H2 20</td>
<td></td>
<td>0.49</td>
<td>0.33</td>
<td>0.99</td>
</tr>
<tr>
<td>H3 20</td>
<td></td>
<td>0.36</td>
<td>0.24</td>
<td>0.99</td>
</tr>
<tr>
<td><strong>Fiskerton</strong></td>
<td><strong>Burial period (months)</strong></td>
<td>1640</td>
<td>1540</td>
<td>1020</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>0.45</td>
<td>0.33</td>
<td>0.99</td>
</tr>
<tr>
<td>12</td>
<td></td>
<td>0.28</td>
<td>0.17</td>
<td>0.85</td>
</tr>
<tr>
<td>18</td>
<td></td>
<td>0.60</td>
<td>0.43</td>
<td>0.99</td>
</tr>
<tr>
<td><strong>Firestone</strong></td>
<td><strong>Burial period (months)</strong></td>
<td>1640</td>
<td>1540</td>
<td>1020</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>0.45</td>
<td>0.31</td>
<td>0.98</td>
</tr>
<tr>
<td>12</td>
<td></td>
<td>0.29</td>
<td>0.20</td>
<td>0.99</td>
</tr>
<tr>
<td>48</td>
<td></td>
<td>0.29</td>
<td>0.18</td>
<td>0.98</td>
</tr>
<tr>
<td><strong>Alum Bay</strong></td>
<td><strong>Burial period (months)</strong></td>
<td>1640</td>
<td>1540</td>
<td>1020</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>0.20</td>
<td>0.12</td>
<td>0.95</td>
</tr>
<tr>
<td>12</td>
<td></td>
<td>0.19</td>
<td>0.11</td>
<td>0.93</td>
</tr>
<tr>
<td>48</td>
<td></td>
<td>0.29</td>
<td>0.18</td>
<td>0.98</td>
</tr>
</tbody>
</table>

The percentage of PII to PI was close to the level of the control sample at Alice Holt with one exception. The sample from H1 buried for 6 months had a much higher percentage PII to PI ratio than any of the other samples. This may have been caused by some localised effect within the environment. Some antler samples also exhibited unexpectedly high variation in weight loss and it would be interesting to investigate if these factors are related. The ratio of PII to mineral indicates whether protein is
degrading relative to the mineral component or whether the mineral component is degrading more rapidly than the protein. The ratio of PII to mineral was higher after both burial periods at the surface burial horizon indicating greater change at depth. The PII to mineral ratios also varied but generally decreased except in the same H1 sample. Firestone experienced gradual changes with decreases in PII to PI and gradual decreases in PII to mineral. The results from Fiskerton differed, in two cases the ratios increased and after twelve months the ratio of PII to PI decreased. The ratio of protein to mineral generally was high except in the sample buried for 12 months, suggesting that the variability within the antler samples was illustrated by the sample recovered after 12 months and also that the PII protein bands were not particularly degraded in this environment during this time period. The PII to mineral ratio also increased which could indicate that the protein is protected within the slightly acidic conditions but the mineral is beginning to deteriorate. The Alum Bay site appears to show by far the greatest amount of protein degradation. The PII to PI ratios are lower and the percentage protein to mineral component is much less.

In unburied antler samples the ratio of PII to PI protein bands was 0.67 and the ratio of PII protein bands to hydroxyapatite was 0.38. The deterioration in the ratio of PII to PI protein bands of the samples from Firestone was only 1% after 3 months and 0.61 after 48 months only 14% higher than the unburied samples. The ratio of PII protein bands to hydroxyapatite was 0.31 after 3 months a decrease of 6% however after 48 months of burial this ratio had decreased to 0.18 a decrease of 20% from the unburied sample. This would suggest that the protein is degrading rapidly in relation to the hydroxyapatite. At Fiskerton the ratio of PII to PI protein bands was 0.74 after 6 months 7% higher than the unburied sample. After 18 months this figure was 0.71 only 4% higher than the
unburied sample indicating that the proteins were hardly degrading over this time period. The ratio of PII protein bands to hydroxyapatite was 0.38 in unburied samples and in the sample recovered from Fiskerton the ratio was 0.33 a decrease of 5%. After burial for 18 months the ratio was 0.43 an increase of 5% in the ratio of PII to hydroxyapatite. This may further indicate the favourable conditions for preservation of proteins at this site. At Alice Holt the ratio of PII to PI protein bands in a sample recovered from Horizon 3 after 20 months was virtually the same as the unburied samples. However the ratio of PII protein bands to hydroxyapatite had changed from 0.38 in unburied samples to 0.24 in the same sample a decrease of 14% in the ratio of protein to hydroxyapatite. At Horizon 1 after a burial period of 20 months samples had a ratio of PII to PI protein bands of 0.83 an increase of 16% whilst the ratio of PII protein bands compared with hydroxyapatite changed from 0.38 in unburied samples to 4.1 in a sample recovered from this horizon an increase of 372% indicating a huge change in mineral to protein ratio. This may well be due to fungal and bacterial activity higher in the soil profile. At Alum Bay the ratio of PII to PI protein bands of samples recovered after 12 months was 0.58 which was 9% lower than unburied samples whilst the ratio of PII protein bands to hydroxyapatite was 0.12 24% less than unburied samples. After 48 months the ratio of PII to PI protein bands was 0.61 a decrease of 6% from unburied samples and the ratio of PII protein bands to hydroxyapatite was 0.18 a decrease of 20% compared with the unburied samples. This would indicate that the site at Alum Bay is prone to protein degradation.
4.5.3. Ivory

The combined FTIR spectra of ivory samples from each of the burial sites and a control sample are shown in Fig.4.41. The spectra of the ivory samples show similar patterns with peaks for protein and for the mineral component hydroxyapatite. The mammoth sample was from an estuarine site at Newtown on the Isle of Wight and aged at 125,000 years. It was used as a comparison with modern ivory. Spectra from the sample of mammoth ivory exhibits much less intense protein peaks than those from the other samples. However even after a burial period of 125,000 years protein is still detectable indicating the durability of the material if burial conditions are favourable. Ivory samples were only buried and recovered from Alum Bay and Firestone. In the environment of Firestone the ratio of the PII to PI protein bands remained virtually unchanged even after 48 months of burial. The ratio of PII to mineral was also relatively unchanged during the period of burial. This would suggest that the protein is not degrading rapidly within this particular burial environment.

Fig. 4.41 Combined FTIR spectra of ivory samples from each of the burial sites and a control sample Key: black; control, purple; Firestone, blue; Alum Bay
The percentage of PII to PI and PII to mineral component are shown in Table 4.9.

**Table 4.9** Relative peak heights above a baseline of ivory samples at specific wavenumbers

<table>
<thead>
<tr>
<th>Firestone</th>
<th>Period(months)</th>
<th>1640</th>
<th>1540</th>
<th>1020</th>
<th>PII:PI</th>
<th>PII:1020</th>
</tr>
</thead>
<tbody>
<tr>
<td>ivory</td>
<td>3</td>
<td>0.37</td>
<td>0.25</td>
<td>0.99</td>
<td>0.67</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>0.41</td>
<td>0.28</td>
<td>0.98</td>
<td>0.68</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>0.41</td>
<td>0.27</td>
<td>0.99</td>
<td>0.68</td>
<td>0.27</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Alum Bay</th>
<th>Period (months)</th>
<th>1640</th>
<th>1540</th>
<th>1020</th>
<th>PII:PI</th>
<th>PII:1020</th>
</tr>
</thead>
<tbody>
<tr>
<td>ivory</td>
<td>3</td>
<td>0.45</td>
<td>0.28</td>
<td>0.99</td>
<td>0.62</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>0.39</td>
<td>0.22</td>
<td>0.98</td>
<td>0.56</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>0.29</td>
<td>0.18</td>
<td>1</td>
<td>0.63</td>
<td>0.18</td>
</tr>
</tbody>
</table>

The ratio of PII to PI protein bands of ivory samples from Firestone was 0.67 after 3 months and 0.68 after 48 months only 7 and 8% respectively higher than the unburied samples. The ratio of PII protein bands to hydroxyapatite was 0.25 after 3 months a decrease of 2%, however after 48 months of burial this ratio was the same as the unburied samples indicating little protein degradation at this site. At Alum Bay the ratio of PII to PI protein bands of samples recovered after 3 months was 0.62 which was a 2% decrease from unburied samples whilst the ratio of PII protein bands to hydroxyapatite was 0.28 a 1% decrease from unburied samples. After 48 months the ratio of PII to PI protein bands was 0.63 a decrease of 3% from unburied samples and the ratio of PII protein bands to hydroxyapatite was 0.18 a decrease of 9% compared with the unburied samples. This would indicate that ivory buried at Alum Bay is susceptible to slow degradation of proteins.
4.5.4. Changes in ratios through time at the reburial sites

The changing ratios of protein and minerals over time at each site are illustrated in Table 4.10. The greatest changes occur in samples at the Alum Bay burial site. This site appears to be the most deteriorating environment for protein. The ratios of PII to PI protein bands was 21% more for horn compared with unburied samples. The ratios for horn at the other sites were reasonably similar at around 12% more than the unburied samples. The Alum Bay site would appear to be responsible for the relatively rapid degradation of protein whilst the mineral fraction of its composition is not so affected. The antler samples at the three terrestrial sites showed only small changes in the ratios of PII to PI protein bands suggesting that protein degradation was slow at these sites. The changing ratio of the antler sample in relation to PII protein bands and hydroxyapatite at Alum Bay is also very high at around 23%.

The next highest loss in protein to mineral of antler samples occurred in samples recovered from Fiskerton with a 14% decrease. At the other two burial sites of Firestone and Alice Holt these ratios were similar at around 5%. At Firestone and Alum Bay the ratio of PII to PI in ivory samples increased slightly whilst the PII to mineral ratios decreased slightly, this could indicate that the protein is degrading preferentially to the mineral. The PII to mineral ratios of antler samples decreased at all of the burial sites but were greatest at the Fiskerton and Alum Bay. If an increase in ratio of PII to PI and a decrease in PII to mineral are used as an indicator of protein degradation then the Alum Bay site can be shown to be the most degrading to protein of the sites used in the study. Ivory appeared to suffer the least deterioration at Alum Bay. Horn would appear to be vulnerable at all of the burial sites, samples showed consistently high levels of protein degradation with the levels at Alum Bay being particularly high. Alum Bay
generally proved to be the site which had the greatest degradation of proteins in all of the materials sampled. The high level of PII protein degradation to hydroxyapatite at Fiskerton (14%) was surprising, it was felt that the hydroxyapatite would be vulnerable to the slightly acidic environment whilst the collagen would be preserved.

**Table 4.10** Changing ratios of protein bands and mineral at the reburial sites

<table>
<thead>
<tr>
<th>Site</th>
<th>Horn</th>
<th>Antler</th>
<th>Ivory</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PII:PI</td>
<td>PII:PI</td>
<td>PII:PI</td>
</tr>
<tr>
<td>Alice Holt</td>
<td>+11.31</td>
<td>+3.24</td>
<td>-5.81</td>
</tr>
<tr>
<td>Fiskerton</td>
<td>+11.83</td>
<td>-1.22</td>
<td>-14.22</td>
</tr>
<tr>
<td>Firestone</td>
<td>+12.27</td>
<td>+1.92</td>
<td>-5.22</td>
</tr>
<tr>
<td>Alum Bay</td>
<td>+21.37</td>
<td>-7.55</td>
<td>-23.31</td>
</tr>
</tbody>
</table>

4.6. **X-Ray diffraction analysis (XRD)**

X-ray diffraction analysis is similarly useful. Fig 4.42 shows the spectra for unburied samples including horn and was used to identify any changes in mineral composition which took place during the period of burial at the reburial sites. Horn has no mineral structure but it was thought that if any mineralisation occurred in the buried horn samples then changes would be recorded in the XRD spectra. XRD spectra of unburied horn, antler and ivory samples are illustrated in Fig. 4.42. The ivory sample spectrum mainly shows hydroxyapatite which is the major mineral component of the material. Ivory is denser structurally than the much more quickly growing antler and is more consistent in composition. The antler sample has two slightly varying mineral crystal structures, hydroxyapatite \([\text{Ca}_{10}(\text{PO}_4)_3(\text{CO}_3)_3(\text{OH})_2]\) and calcium phosphate carbonate \([\text{Ca}_{10}(\text{PO}_4)_6\text{CO}_3]\), which are slightly different in composition. The quickly growing antler exhibits a slightly less homogenous and crystalline structure in comparison to ivory. The only peaks visible on the horn spectra relate to silicon carbide from the
abrasive initially used to powder it. This is indicative of the lack of crystalline structure within the material.

The ivory and antler samples exhibit quite closely matching spectra which is unsurprising considering their similarity in mineral composition, however the differences detected in the x-ray diffraction spectra could be used to identify the materials. The horn sample has a number of small peaks. These were identified as silicon carbide which had been introduced into the sample by the silicon carbide powder used to abrade it into powder in preparation for analysis. Otherwise the horn has no apparent crystalline structure. On interpretation of the spectra, if the same compound (peak) appears in several samples it is not possible to compare the heights of those peaks and make conclusions about the intensity/amount of that compound or the extent of deterioration between the different samples. This is because the intensity of each peak is only relative to the peaks in each individual scan i.e. the influence of silicon carbide on the intensities is high and there will also be soil (quartz) in the sample that affects the intensity.

![Graph](image)

**Fig. 4.42** Combined X-ray diffraction spectra of antler, (red), ivory, (green) and horn, (blue), unburied samples

X-ray diffraction spectra of samples of antler and horn recovered from the Alice Holt burial site are shown below in Figs 4.43 and 4.44 respectively.
**Alice Holt:** Antler (Horizons 1 to 3) 6 and 20 months

![Graph showing XRD scan results for various horizons.](image)

<table>
<thead>
<tr>
<th>Colour on graph</th>
<th>Powder Diffraction File (PDF)</th>
<th>Mineral name</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>22-1273</td>
<td>Silicon Carbide</td>
<td>SiC</td>
<td></td>
</tr>
<tr>
<td>19-272</td>
<td>Carbonatehydroxylapatite</td>
<td>Ca₁₀(PO₄)₃(CO₃)₃(OH)₂</td>
<td></td>
</tr>
<tr>
<td>35-180</td>
<td>Calcium Phosphate Carbonate</td>
<td>Ca₁₀(PO₄)₆CO₃</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Horizon</th>
<th>Depth (m)</th>
<th>Months burial</th>
<th>XRD Scan</th>
<th>Colour on Graph</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.1</td>
<td>6</td>
<td>AH12.6</td>
<td>Red</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>7094</td>
<td>Grey</td>
</tr>
<tr>
<td>2</td>
<td>-0.38</td>
<td>6</td>
<td>AH10.6</td>
<td>Blue</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>7093</td>
<td>Brown</td>
</tr>
<tr>
<td>3</td>
<td>-0.9</td>
<td>6</td>
<td>AH8.6</td>
<td>Green</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>7092</td>
<td>Light Blue</td>
</tr>
</tbody>
</table>

**Fig. 4.43** Alice Holt Antler Horizons 1 to 3 recovered after 6 months and 20 months

**Horn:** (Horizons 1 to 3) 6 and 20 months
The Horn samples from Alice Holt shown in Fig. 4.44 illustrate the lack of crystal structure the only crystals detected were from silicon carbide which was the abrasive used to prepare the samples.
Fig. 4.45 shows the X-ray diffraction spectra of antler samples recovered from Fiskerton. Minerals identified were silicon carbide, SiC, which originates from the abrasive paper used in powdering the samples prior to analysis, carbonate hydroxylapatite \([\text{Ca}_{10}(\text{PO}_4)_3(\text{CO}_3)_3(\text{OH})_2]\) and calcium phosphate carbonate \([\text{Ca}_{10}(\text{PO}_4)_6\text{CO}_3]\), both from the composition of the mineral. At Fiskerton the diffraction patterns produced by the antler samples shown in Fig. 4.45 also showed peaks for silicon carbide similar to those produced by the horn samples shown in Fig. 4.46. The antler samples have peaks corresponding to the minerals, carbonate hydroxylapatite and calcium phosphate carbonate, relating to the mineral composition of the material. There appears to be little difference between the spectra of samples recovered from different burial periods with no other minerals detected.
Fiskerton: Antler

Fig. 4.45 X-ray diffraction spectra of antler samples recovered after burial at Fiskerton for 6 months (red), 12 months (blue) and 18 months (green)
**Fiskerton: Horn**

**Fig. 4.46** X-ray diffraction spectra of horn samples recovered after burial at Fiskerton for 6 months (red), 12 months (blue) and 18 months (green)

<table>
<thead>
<tr>
<th>Colour on graph</th>
<th>Powder Diffraction File (PDF)</th>
<th>Mineral name</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>22-1273</td>
<td>Silicon Carbide</td>
<td>SiC</td>
<td></td>
</tr>
</tbody>
</table>

The horn samples from Fiskerton showed similar results as those from Alice Holt with the only crystal structures detected being from the silicon carbide paper used in the preparation of the samples.
Firestone

X-ray diffraction spectra of antler samples recovered after burial at the Firestone site for 3, 12 and 48 months are illustrated in Fig. 4.47, which show in order of magnitude detected, magnesioferrite \([\text{MgFe}^{3+} \text{O}_4]\), carbonatehydroxylapatite \([\text{Ca}_{10}(\text{PO}_4)_3(\text{CO}_3)_3(\text{OH})_2]\). There were also traces of calcium phosphate carbonate \([\text{Ca}_{10}(\text{PO}_4)_6\text{CO}_3]\).

The minerals which form part of the natural structure of antler are the carbonatehydroxylapatite and the calcium phosphate carbonate. The presence of magnesioferrite is very interesting. This is an unusual mineral but not unknown. The mineral must have been introduced onto the sample from the surrounding burial environment.

The X-ray diffraction spectra of ivory samples recovered from Firestone are shown in Fig. 4.54. The spectra illustrate the presence of the structural mineral hydroxyapatite and also the silicon carbide used in the preparation of the samples. Magnesioferrite was not detected on the surface of the ivory samples from this site unlike the antler samples where it was detected on the surface.

The X-ray diffraction spectra of horn samples recovered from Firestone are shown in Fig. 4.48. The only mineral detected was once again the silicon carbide which was used in the preparation of the samples.
**Firestone: Antler**

![X-ray diffraction spectra](image)

<table>
<thead>
<tr>
<th>No.</th>
<th>Visible</th>
<th>Ref. Code</th>
<th>Compound Name</th>
<th>Chemical Formula</th>
<th>Score</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>True</td>
<td>00-001-1120</td>
<td>Magnesioferrite</td>
<td>Mg Fe^{3+}_2 O_4</td>
<td>21</td>
</tr>
<tr>
<td>2</td>
<td>True</td>
<td>00-019-0272</td>
<td>Carbonatehydroxylapatite, syn</td>
<td>Ca_{10}(PO_4)_{3}(CO_3)(OH)_2</td>
<td>12</td>
</tr>
<tr>
<td>3</td>
<td>True</td>
<td>00-022-1273</td>
<td>Moissanite-6H, syn</td>
<td>Si C</td>
<td>54</td>
</tr>
<tr>
<td>4</td>
<td>False</td>
<td>00-035-0180</td>
<td>Calcium Phosphate Carbonate</td>
<td>Ca_{10}(PO_4)_{6}CO_3</td>
<td>10</td>
</tr>
</tbody>
</table>

**Fig. 4.47** X-ray diffraction spectra of antler samples recovered after burial at Firestone for 3 months (red), 12 months (blue) and 48 months (green)
Firestone: Horn

<table>
<thead>
<tr>
<th>No</th>
<th>Ref. Code</th>
<th>Compound Name</th>
<th>Chemical Formula</th>
<th>Score</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>00-022-1273</td>
<td>Moissanite-6H, syn</td>
<td>Si C</td>
<td>57</td>
</tr>
</tbody>
</table>

**Fig. 4.48** X-ray diffraction spectra of horn samples recovered after burial at Firestone for 3 months (red), 12 months (blue) and 48 months (green)
Firestone: Ivory

**Fig. 4.49** X-ray diffraction spectra of ivory samples recovered after burial at Firestone for 3 months (red), 12 months (blue) and 48 months (green)
Alum Bay

X-ray diffraction spectra of antler samples recovered after burial for 3, 12, and 48 months at Alum Bay are illustrated in Fig. 4.50 showing, magnesioferrite which is illustrated by the grey bars $\text{MgFe}^{3+}_2\text{O}_4$, which is probably from the surrounding burial environment. Carbonatehydroxylapatite $\text{Ca}_{10}(\text{PO}_4)_3(\text{CO}_3)_3(\text{OH})_2$, and calcium phosphate carbonate $[(\text{Ca}_{10}(\text{PO}_4)_6\text{CO}_3]$ were also detected which is the mineral component of the antler itself. Magnesioferrite was also detected on antler samples from Firestone. Interestingly Alum Bay and Firestone are within the Solent system though Alum Bay is fully marine whilst Firestone is estuarine and brackish.

X-ray diffraction spectra of ivory samples recovered from Alum Bay are illustrated in Fig. 4.52. The spectra are again similar to those of samples from Firestone. The only minerals being detected are hydroxyapatite the mineral component of the ivory itself and silicon carbide from the abrasive used to prepare the samples. Magnesioferrite was not detected in the same way it was undetected on ivory samples recovered from Firestone.

X-ray diffraction spectra of horn samples recovered from Alum Bay are illustrated in Fig. 4.51. They exhibit similar spectra to horn samples recovered from the other burial sites in that the only mineral detected is silicon carbide which has been introduced to the sample from the abrasive used to prepare them for analysis.
### Alum Bay: Antler

#### Fig. 4.50

X-ray diffraction spectra of antler samples recovered after burial at the marine site for 3 months (red), 12 months, (blue), 48 months (green)

<table>
<thead>
<tr>
<th>No</th>
<th>Ref. Code</th>
<th>Compound Name</th>
<th>Chemical Formula</th>
<th>Score</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>Magnesioferrite</td>
<td>Mg Fe$^{3+}$ O4</td>
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<tr>
<td>2</td>
<td>00-019-0272</td>
<td>Carbonatehydroxylapatite, syn</td>
<td>(PO4)3(CO3)3(OH)2Ca10</td>
<td>22</td>
</tr>
<tr>
<td>3</td>
<td>00-022-1273</td>
<td>Moissanite-6H, syn</td>
<td>Si C</td>
<td>46</td>
</tr>
<tr>
<td>4</td>
<td>00-035-0180</td>
<td>Calcium Phosphate Carbonate</td>
<td>Ca10(PO4)6CO3</td>
<td>29</td>
</tr>
</tbody>
</table>
Alum Bay: Horn

**Fig. 4.51** X-ray diffraction spectra of horn samples recovered after burial at the marine site for 3 months (red), 12 months, (blue), 48 months (green)

<table>
<thead>
<tr>
<th>No</th>
<th>Ref. Code</th>
<th>Compound Name</th>
<th>Chemical Formula</th>
<th>Score</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>00-022-1273</td>
<td>Moissanite-6H, syn</td>
<td>Si C</td>
<td>40</td>
</tr>
</tbody>
</table>
**Alum Bay: Ivory**

![X-ray diffraction spectra](image)

<table>
<thead>
<tr>
<th>No.</th>
<th>Visible</th>
<th>Ref. Code</th>
<th>Compound Name</th>
<th>Chemical Formula</th>
<th>Score</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>True</td>
<td>00-001-1008</td>
<td>Hydroxyapatite</td>
<td>$\text{Ca}_{10}(\text{PO}_4)_3(\text{CO}_3)_3(\text{OH})_2$</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>True</td>
<td>00-022-1273</td>
<td>Moissanite-6H, syn</td>
<td>$\text{Si C}$</td>
<td>6</td>
</tr>
</tbody>
</table>

**Fig. 4.52** X-ray diffraction spectra of ivory samples recovered after burial at the marine site for 3 months (red), 12 months, (blue), 48 months (green)
4.6.1. Summary of X- Ray diffraction studies

XRD can be used to identify the minerals present, but to do this accurately requires information on all the likely degradation products and contaminants. It was thought that the technique may have been useful in investigating samples such as that of the bison horn and horn from the marine environment where the FTIR spectra indicate the presence of unidentified mineral products which are not present on other samples from the same sites.

Whilst there were few changes to the mineral structure of the buried and recovered samples from the other burial sites there was a potentially significant change in antler samples recovered from Firestone and Alum Bay. The samples showed the presence of magnesioferrite a compound consisting of magnesium and iron. This compound did not appear on the other samples. However strong peaks for iron were observed on EDAX analysis for antler samples recovered from Firestone and from Alum Bay. Intense iron peaks were also observed on EDAX analysis of antler samples from Fiskerton but these did not appear in the XRD analysis of samples from this site. Horn samples from Fiskerton showed intense peaks for iron as well as did samples from Firestone, these also did not appear on the XRD analysis for horn. The appearance of magnesioferrite on antler samples from the Firestone and Alum Bay is interesting as this is quite an unusual mineral.

4.7. Biochemical studies

The aims of the experiments were to isolate the dominant organisms present in the sample material and to explore the ability of those organisms to attack the main components of those materials. Traditional techniques were employed to accomplish
these aims. The following studies were undertaken on antler and ivory samples only.

4.7.1 Enzyme assays

A protease from *Bacillus licheniformis*, was used in experiments with a chromogenic substrate to establish the efficiency of the enzyme at diffusing through various nutrient media. The first experiments contained purchased collagen to provide reference data and then powdered antler and ivory were mixed with various media to compare with the purchased collagen. The extent of enzyme diffusion through collagen and nutrient agar media is shown below in Fig.4.53. The plates were either injected with the enzyme or it was dropped onto the surface or pipette into pre formed 2 mm diameter wells cut into the surface of the media in a dilution series with concentrations of $10^0$, $10^{-1}$ and $10^{-2}$. The experiment successfully illustrated that the majority of samples from each site and from different burial periods were capable of growing cultures on growth media prepared with collagen.

Fig. 4.53 Results of the initial experiment using three concentrations of the protease, *Bacillus licheniformis*
The experiment was refined and repeated using an extended dilution series and increased amount of the protease to measure how efficient it was at diffusing through media containing powdered antler and powdered ivory and the chromogenic substrate to produce calibration curves. Growth halos were clearly visible around the cut wells in the media where the protease was injected these are shown in Fig. 4.54. The diameters of the halos on each of the plates was measured in order to produce calibration curves these were then graphed and subjected to a regression analyses to establish the efficiency of the protease at diffusing through each type of media.

![Antler](image1) ![Collagen](image2) ![Ivory](image3)

**Fig. 4.54** Growth halos illustrating the diffusion of the protease from *Bacillus licheniformis* through agar containing collagen, ivory and antler powders after incubation for 24 hours at 22°C

This experiment produced positive results showing that the method worked with all of the media and produced smaller halos as the dilutions increased. The results are
illustrated graphically in Figs. 4.55 and 4.56. The results were graphed linearly with a regression calculation, to express the extent of correlation between the culture media and the enzyme. Strong correlation behaves linearly therefore a strong correlation would allow calibration to take place. The highest correlation indicates the best fit and so it can be used for calibration. The values which are near 1 show strong correlation, meaning that the media and material are linked. If the value is 0 then there is no correlation between the factors.

![Graphs illustrating correlation between culture media and enzyme](image)

**Fig. 4.55** Enzyme diffusion through a chromogenic substrate with nutrient agar media. Dashed line antler, solid line collagen, dotted line ivory

In the initial experiment Nutrient Agar 1, the greatest correlation occurred using the enzyme with purchased collagen with the other 2 materials having slightly less correlation. In the second experiment Nutrient Agar 2 the media containing antler
powder had the highest correlation with less variation between the medias containing collagen and ivory. In both experiments the collagen, powdered ivory and powdered antler showed that they had a strong correlation with the media. Different agars were used as they contain varying amounts of nutrients and would affect the ability of the protease to utilise the media in a manner which could be measured.

![Graphs showing enzyme diffusion through a chromogenic substrate with different media](image_url)

**Fig. 4.56** Enzyme diffusion through a chromogenic substrate with 10% nutrient agar media, and with technical agar. Antler (dashed), collagen (solid), and ivory (dotted)

The media made with technical agar had the least correlation with purchased collagen, but a fairly strong correlation with antler and particularly with ivory. Table 4.11 shows the regression values illustrating the correlation between the enzyme and various culture media. This would suggest that the powdered antler and ivory contained sufficient a sufficient amount of collagen for it to be used by the enzyme.
Table 4.11 Regression values of the diffusion of an enzyme through various cultural media.

<table>
<thead>
<tr>
<th>Culture medium</th>
<th>Regression value for culture medium prepared with:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Collagen</td>
</tr>
<tr>
<td>Nutrient agar (1)</td>
<td>0.9085</td>
</tr>
<tr>
<td>Nutrient agar (2)</td>
<td>0.9443</td>
</tr>
<tr>
<td>1:10 nutrient agar</td>
<td>0.4339</td>
</tr>
<tr>
<td>Technical agar</td>
<td>0.2975</td>
</tr>
</tbody>
</table>

4.7.2. Analysis of sample materials

A plate assay was undertaken to establish whether samples of antler and ivory both unburied and buried within the various reburial sites contained microorganisms which degraded collagen. Media were prepared with nutrient agar which was dyed with a chromogenic substrate. If protein was degraded a discolouration was produced around the point where the sample was introduced into the media if organisms were present. The results demonstrated that the majority of the samples produced microbial cultures suggesting that microbes were present on the samples and also in soil washed from the surface of the samples.

4.7.3. Gram staining

Colonies were next isolated for gram staining. The colonies selected for gram staining were from antler and ivory samples. The antler sample came from Alice Holt and had been recovered after burial for a period of 18 months. The ivory sample came from Firestone where it had been recovered after a burial period of 48 months. These two samples had produced the most defined cultures when grown through a dilution series. The antler sample came from Alice Holt and was recovered after 18 months of burial. It was cultured on a media consisting of nutrient agar and antler powder. The ivory sample was recovered from Firestone after 48 months of burial. Three colonies were isolated from the antler sample assay and the isolated cultures were grown on individual plates.
containing nutrient agar and the chromogenic substrate. Two colonies were isolated from the ivory sample and treated in a similar way to the antler sample. The isolated cultures were then gram stained and photographed using light microscopy. The results are illustrated in Fig.4.57. The selected colonies from the antler sample produced sample A, Gram-negative coccobacilli, G, Gram-positive coccus, M, short Gram-positive rods coryneform. The colonies from the ivory sample produced F, Gram-positive short rods and N, taken from soil on the sample surface, Gram-positive short rods. A summary of the isolated and cultured samples is set out in Table 4.12.

**Table 4.12** Source and isolation of bacteria from media containing powdered ivory or antler

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Source</th>
<th>Sample No.</th>
<th>Dilution</th>
<th>Medium</th>
<th>Selected colony</th>
<th>Bacteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antler</td>
<td>Alice Holt: 18 months</td>
<td>S14</td>
<td>10^-2</td>
<td>Antler and nutrient agar</td>
<td>A</td>
<td>Gram-coccobacilli</td>
</tr>
<tr>
<td>Ivory</td>
<td>Firestone: 48 months</td>
<td>S14</td>
<td>10^-2</td>
<td>Ivory and nutrient agar</td>
<td>F</td>
<td>Gram+ short rods</td>
</tr>
<tr>
<td>Antler</td>
<td>Alice Holt: 18 months</td>
<td>S14</td>
<td>10^-2</td>
<td>Antler and nutrient agar</td>
<td>G</td>
<td>Gram+ coccus</td>
</tr>
<tr>
<td>Antler</td>
<td>Alice Holt: 18 months</td>
<td>S14</td>
<td>10^-2</td>
<td>Antler and nutrient agar</td>
<td>M</td>
<td>Short Gram+ coryneform rods</td>
</tr>
<tr>
<td>Ivory (soil)</td>
<td>Firestone: 48 months</td>
<td>S14</td>
<td>10^-2</td>
<td>Nutrient agar</td>
<td>N</td>
<td>Gram+ short rods</td>
</tr>
</tbody>
</table>
Fig. 4.57 Images of Gram-stained bacteria under light microscopy, taken from ivory or antler samples retrieved from the reburial sites (a; A, (b) F; (c) G; (d) M; (e) N)
4.7.4. Summary of Biochemical studies

The biochemical studies were interesting in a number of ways. It was shown that an enzyme from *Bacillus licheniformis* was able to attack collagen in an agar diffusion test. This enzyme affected both powdered antler and ivory which was labelled with a dye. A relationship between halo size and the concentration of the enzyme was proven. Traditional microbiological techniques were employed to isolate organisms which were subsequently Gram stained and recorded using light microscopy. Unfortunately due to time pressure there was no time to investigate the isolates to establish whether they were capable of collagenase production. Bacteria were detected on samples recovered from the reburial sites by using media containing a chromogenic substrate which discolours when protein degrading enzymes are present (Ten, 2004). Protein degrading enzymes were identified in recovered antler and ivory samples, indicating the potential for protein degradation by bacteria. It would be useful to extend these studies to include horn samples in order to establish if keratin is attacked by bacteria. It would also be interesting to test for the presence of fungi and *Actinomycetes*, as both are known to degrade proteins. The application of molecular techniques on isolated cultures would enable particular species of bacteria to be identified.

Soil samples could be screened to isolate particular groups of bacteria by using specific chromogenic substrates. The impact of variations caused by seasonality and naturally occurring changes to bacteria within the environments themselves could be investigated.
4.8. Evaluation of techniques to monitor material change

The environment provides the context within which chemical, physical and biological processes occur which cause the deterioration of materials. Samples were examined using a variety of analytical techniques to provide a wide range of data regarding the types of degradation taking place on the materials. One of the purposes of the analytical evaluation was to establish whether variations in the condition of the recovered samples could be attributable to parameters that have been monitored and recorded within the environment. The techniques used in the study and the type of deterioration they were used to evaluate are set out in Table 4.13.

Table 4.13 Analytical techniques used in the study and characteristics they were designed to evaluate

<table>
<thead>
<tr>
<th>Type of Deterioration</th>
<th>Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical</td>
<td>EDAX</td>
</tr>
<tr>
<td>Chemical/Biological</td>
<td>FTIR</td>
</tr>
<tr>
<td>Chemical</td>
<td>XRD</td>
</tr>
<tr>
<td>Physical/Biological</td>
<td>SEM</td>
</tr>
<tr>
<td>Biological</td>
<td>Microbiology</td>
</tr>
</tbody>
</table>

4.8.1. SEM and EDAX

Evaluation of physical deterioration from SEM images is useful but qualitative. Physical deterioration can be observed and then it can be described. However there is no recognised terminology to standardise the observations made. The SEM can observe physical changes over time by looking at samples at extremely high levels of
magnification, which enables physical deterioration to be observed. SEM is also very useful for identifying samples that are biodegrading. The high levels of magnification achieved by the SEM are capable of showing bacteria on the surfaces of samples. The use of SEM was particularly useful in this study where bacteria were observed on a number of samples from various sites.

There is no recognised descriptive language to describe the physical manifestation of weathering on these types of materials. Therefore damage indicators were devised after observing characteristic features of deterioration on the surfaces of unburied, and buried and recovered samples from the various reburial sites.

The high level of magnification of the SEM enabled the presence of bacteria to be observed on a number of samples. This suggests that bacteria may be degrading protein in the samples. An increase in surface weathering would make the samples more vulnerable to further bacterial attack and penetration. The cracked surfaces particularly on the ivory samples would also make them very vulnerable to further deterioration on drying. The damage indicators are a rough method of describing physical deterioration but they provide relevant information which is useful when added to the data provided by other analytical techniques.

With an increase in time of recovery both horn and antler samples from Alice Holt experienced an increase in the total amount of observable deterioration. Antler recovered from Fiskerton also showed an increase in the amount of observable deterioration, as did ivory samples at Firestone and at Alum Bay. There was a decrease in the observable amount of deterioration of horn at Fiskerton and of both antler and horn at Firestone and Alum Bay.
The significant elements on the surface of unburied control samples were recorded by EDAX analysis and noted in order to observe any changes in elemental composition taking place over the burial period. Unburied samples of, horn, antler and ivory were first analysed to establish their elemental composition. The surface elements recorded by EDAX analysis were as follows;

- Horn, sulfur
- Antler, calcium, phosphorus
- Ivory, calcium, phosphorus.

The elements recorded are those which would be expected in these materials, the sulfur illustrates the disulfide bonding of the keratin molecules within the horn samples, and the calcium and phosphate in antler and ivory samples, relates to the mineral component of their structure.

It may prove possible to statistically analyse the surface element changes over time in an effort to understand whether there is a methodology and a sequence to changes taking place on the surface at different sites at different periods, or to show whether particular sequences can be related to specific site environments. The EDAX used in the study did not have the capability of accurately measuring the percentage composition of elements recorded but it is possible with modern analytical equipment.

Perhaps the most significant elemental changes recorded by EDAX analysis are changes in levels of both iron and sulfur on the surface of various samples. These elements were not present on the surface of any of the control samples but occur on some of the recovered samples.
4.8.2. Weight Loss

Weight loss provides an overview and a general picture of the decay of a sample. It is very useful for looking at sample material for a number of reasons. The technique is simple to carry out and effective at producing data relating to the amount of deterioration. The results, expressed as a percentage are directly comparable with material from different sites and from varied burial periods. The ability to assess degradation occurring through time is very useful for assessing the potential of a particular site to protect or degrade material buried in it. Weight loss data has the potential to allow predictions to be made regarding the length of time that materials will take to become completely deteriorated in different environments. Accuracy is not possible with the amount of data available in this study but the potential for predicting deterioration over time is a realistic objective. To be able to predict the amount of weight loss and ultimately the length of time that an object would take to deteriorate completely in a particular burial environment would require data obtained over a longer period of time.

It is also possible to interpolate the weight loss at intervals where samples have not been retrieved by graphing the weight loss and taking readings off graphs in between the data points. In this way the weight loss throughout the burial period at each site can be interpreted. The graphed weight loss of a number of selected samples is illustrated in Fig. 4.58 to illustrate the principle. The horn sample from Alum Bay showed the greatest weight loss of all samples from any of the sites illustrated in Fig. 4.59. Even by graphing the results logarithmically and by stretching the time axis the data cannot predict the time when the sample would be totally degraded. The graphs predict slowly increasing weight loss generally, but predict a slight decrease in weight loss of antler...
samples from Alice Holt after burial for 48 months. To predict the behaviour of the weight loss of the materials more accurately longer burial periods are required by doing this the amount of degradation should be predictable if the environment does not change.

**Fig. 4.58** Weight loss of horn, antler and ivory at Alice Holt and Fiskerton and the predicted weight loss after a burial period of 48 months
Horn Alum Bay

Fig. 4.59 Weight loss of horn, ivory at Alum Bay and the predicted weight loss after an extended burial period

The use of differential equations would allow other factors which affect the deterioration of the materials to be taken into consideration. A mathematical model could then be constructed which could predict the weight loss at certain times in the future. However this is extremely complex and would require methods of extrapolating the data which necessitate the making of a number of simplifying assumptions. A differential equation looks at the rate of change through time.

4.8.3. FTIR

FTIR analysis can be used to characterise the state of degradation of antler. A distinction can be made between areas between wavenumbers 1350 cm\(^{-1}\) and 1700 cm\(^{-1}\) there are four peaks which correspond to collagen protein and the range between wavenumber 800 cm\(^{-1}\) and 1000 cm\(^{-1}\) is specific to peaks of carbonate and phosphate salts. The marine site at Alum Bay proved to be the most susceptible of all the burial sites to protein degradation for all of the materials. This is of interest in that skeletal
materials including bone are generally considered to be well preserved in marine environments particularly if a site becomes rapidly anaerobic.

Mineralisation of the material was not expected over the short period in which the samples had been buried. In sub-fossil bone it is generally considered that there is a loss of protein with no consequent mineralization from geologic sources in the burial environment, (Shelton and Johnson, 1995). The relationships between protein and mineral content are very interesting. The ratios and intensities of the peaks were produced in a standard format to allow comparisons to be made. This was achieved in this study by using facilities available in the software of the spectrometer. Spectra were first smoothed and processed then normalised to produce spectra which could be directly compared with each other. It is possible however to calculate peak intensities directly from a baseline on unprocessed spectra. This would allow peak intensities to be calculated from actual values rather than values which have been adjusted by the computer software. The data obtained to date would benefit from further interrogation. In the study proteins were measured at specific wavenumbers within the spectra and classed as PII and PI to differentiate them. There are more Amide bands within the peaks studied and their proportions measured against each other would be helpful in determining the amount of protein degradation which is taking place and exactly where this degradation is taking place within the secondary structure of the proteins. FTIR is an extremely useful tool in the examination of organic materials.

4.8.4. XRD

Horn is not a mineral so XRD was not able to identify any structure within it. XRD was successful in identifying the differences in mineral composition between ivory and antler, which are subtle but important ways of differentiating the two materials. The use
of x-ray diffraction in the examination of the samples did show up the addition of an iron bearing compound on some surfaces. The mineral was magnesioferrite and it appeared on samples from Firestone and Alum Bay. Interestingly these sites are both in the Solent estuarine system and this unusual mineral may be particular to this area. XRD can be used to identify what is there, but to do this accurately, information on all the likely degradation products, contaminants, is required. The technique may be useful in investigating samples such as that of the bison horn and cattle horn from the marine environment where the FTIR spectrographs indicate unidentified mineral products which are not present on other samples from the same sites.
CHAPTER 5

GENERAL DISCUSSION AND CONCLUSIONS

5.1. Introduction

The materials selected for use in this study are not necessarily likely to be found on archaeological excavations. Ivory in particular is a high status material which is rarely found. The materials though have all been utilised since the earliest times. They were used in this study because they are organic and contain proteins and any changes could be compared and analysed and then related to the different environments in which they had been buried. The processes of deterioration are complex and encompass physical, chemical and biological mechanisms and combinations of all three. The rates and processes of deterioration are determined by the nature of the burial environment. The only type of environment in which it might be possible for all three materials to survive in the medium to long term would be a waterlogged environment with a neutral pH. The study site most closely resembling these conditions used in this study was the brackish wetland at Firestone Copse. By comparing conditions and material degradation it was possible to establish whether this site was less degrading to the materials than the other sites studied.

5.2. Interactions of deterioration factors

The general approach of using a number of analytical techniques to investigate the deterioration of organic materials recovered from different burial environments has been useful. The results have shown that deterioration of the buried samples has occurred. The monitoring of environmental conditions illustrates the differences in the burial
environments from which the samples were recovered. The next step is to explore whether the types of deterioration are related and how they affect each other and then to investigate whether the environmental conditions can be directly related to specific types and rates of degradation in particular materials. To do any modelling of the deterioration of materials in the environment, it would be necessary to measure the impact of any changes observed.

An attempt to combine the type and amount of deterioration which occurred in the samples was undertaken using the environmental monitoring data obtained from the sites and from data recorded by the various analytical techniques. A mean figure of combined total deterioration was calculated for the horn samples. For example, the sites mean Eh potential was used by ranking the most reduced site at 1 as it would theoretically be the most protective. Similarly the site with a pH nearest to 7 was ranked as 1 as this would be the most protective. The ratios of PII to PI and PII to mineral were measured as the percentage variation from the control samples. The combined results of sample deterioration incorporating environmental factors and other analytical results for horn sample are shown in Table 5.1. A mean figure of combined total deterioration was then calculated for the samples. The mean was calculated by adding the deterioration figures and dividing by the number of sites. The environmental data at Firestone was not contemporary with the burial period of the sample material so it cannot be directly compared with the deterioration on the recovered samples. To avoid confusion the environmental results for Firestone have not been entered in the tables.
Table 5.1 Combined results of sample deterioration found on horn samples incorporating environmental factors and other analytical results

<table>
<thead>
<tr>
<th>Site/material Horn</th>
<th>Mean Eh</th>
<th>Mean pH</th>
<th>Ratio PII/PI %</th>
<th>Mean Weight loss %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alice Holt</td>
<td>125</td>
<td>6.85</td>
<td>+11.31</td>
<td>21.76</td>
</tr>
<tr>
<td>Fiskerton</td>
<td>-36</td>
<td>6.46</td>
<td>+11.83</td>
<td>11.75</td>
</tr>
<tr>
<td>Firestone</td>
<td>-</td>
<td>-</td>
<td>+12.27</td>
<td>12.36</td>
</tr>
<tr>
<td>Alum Bay</td>
<td>-</td>
<td>-</td>
<td>+21.37</td>
<td>24.65</td>
</tr>
</tbody>
</table>

The ranking of the burial site in respect of the amount of deterioration caused to horn samples shown in Table 5.2.

Table 5.2 The ranking of deterioration of horn samples from each reburial site 1, protective, 4 degrading

<table>
<thead>
<tr>
<th>Site/material Horn</th>
<th>Mean Eh</th>
<th>Mean pH</th>
<th>Ratio PII/PI %</th>
<th>Mean Weight loss %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alice Holt</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Fiskerton</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Firestone</td>
<td>-</td>
<td>-</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Alum Bay</td>
<td>-</td>
<td>-</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

The combined results of sample deterioration incorporating environmental factors and other analytical results for antler samples are shown in Table 5.3.
Table 5.3 Combined results of sample deterioration found on antler samples incorporating environmental factors and other analytical results

<table>
<thead>
<tr>
<th>Site/material</th>
<th>Antler</th>
<th>Mean Eh</th>
<th>pH</th>
<th>Ratio PII/P I %</th>
<th>Ratio PII/mineral %</th>
<th>Mean Weight loss %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alice Holt</td>
<td>125</td>
<td>6.85</td>
<td>+3.24</td>
<td>-5.81</td>
<td>21.03</td>
<td></td>
</tr>
<tr>
<td>Fiskerton</td>
<td>-36</td>
<td>6.46</td>
<td>-1.22</td>
<td>-14.22</td>
<td>15.03</td>
<td></td>
</tr>
<tr>
<td>Firestone</td>
<td>-</td>
<td>-</td>
<td>+1.92</td>
<td>-5.22</td>
<td>16.86</td>
<td></td>
</tr>
<tr>
<td>Alum Bay</td>
<td>-</td>
<td>-</td>
<td>-7.55</td>
<td>-23.31</td>
<td>14.42</td>
<td></td>
</tr>
</tbody>
</table>

The ranking of the burial site in respect of the amount of deterioration caused to antler samples shown in Table 5.4.

Table 5.4 The ranking of deterioration of antler samples from each reburial site 1, protective, 4 degrading

<table>
<thead>
<tr>
<th>Site/material</th>
<th>Antler</th>
<th>Mean Eh</th>
<th>Mean pH</th>
<th>Mean Ratio PII/P I %</th>
<th>Mean Ratio PII/mineral %</th>
<th>Mean Weight loss %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alice Holt</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Fiskerton</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Firestone</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Alum Bay</td>
<td>-</td>
<td>-</td>
<td>4</td>
<td>4</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

The exercise was repeated using data obtained from recovered ivory samples. These were only buried at two sites for logistical reasons. The combined results of sample deterioration incorporating environmental factors and other analytical results for ivory
samples are shown in Table 5.5. The ranking of the burial site in respect of the amount of deterioration caused to ivory samples is shown in Table 5.6.

**Table 5.5** Combined results of sample deterioration found on ivory samples incorporating environmental factors and other analytical results

<table>
<thead>
<tr>
<th>Site</th>
<th>Mean Eh</th>
<th>pH</th>
<th>Damage</th>
<th>Mean Ratio PII/PI %</th>
<th>Mean Ratio PII/mineral %</th>
<th>Mean Weight loss %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brackish</td>
<td>-</td>
<td>-</td>
<td>4.66</td>
<td>+7.47</td>
<td>-0.48</td>
<td>13.48</td>
</tr>
<tr>
<td>Marine</td>
<td>-</td>
<td>-</td>
<td>5.66</td>
<td>+0.72</td>
<td>-4.5</td>
<td>14.42</td>
</tr>
</tbody>
</table>

**Table 5.6** The ranking of deterioration of ivory samples from each reburial site 1, protective, 2 degrading

<table>
<thead>
<tr>
<th>Site/material</th>
<th>Mean Eh</th>
<th>Mean pH</th>
<th>Damage</th>
<th>Mean Ratio PII/P I %</th>
<th>Mean Ratio PII/mineral %</th>
<th>Mean Weight loss %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ivory</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brackish</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Marine</td>
<td>-</td>
<td>-</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

The overall ranking of the greatest deterioration occurring on each type of sample material at each particular burial site is summarised in Table 5.7, with 1 the least deteriorated and 4 the most deteriorated.
Table 5.7 Overall ranking of deterioration of each type of sample material at each of the reburial sites

<table>
<thead>
<tr>
<th>Site</th>
<th>Horn</th>
<th>Antler</th>
<th>Ivory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alice Holt</td>
<td>3</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>Fiskerton</td>
<td>2</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>Firestone</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Alum Bay</td>
<td>4</td>
<td>4</td>
<td>2</td>
</tr>
</tbody>
</table>

The methodology is useful for predicting the deterioration of the samples as the factors used in the calculations take into account the varied nature of the materials. The Alum Bay site is the most degrading of all of the burial sites used in the study whilst Firestone is the most protective. Firestone behaves in the way which could have been predicted (Watkinson, 1987). It has a reduced environment with a pH around neutral which would preserve the majority of organic materials. The marine site would be expected to have better preservation of antler and ivory. The disappearance of horn nocks from the site of the Mary Rose looks less surprising when the rapidity of the degradation of horn at the marine burial site is noted.

Table 5.8 is adapted from Table 1.1 Watkinson 1987, where the predictions for material survival have been adapted to the sites and materials used in the study.
Table 5.8 Environmental conditions at the burial sites and the predicted likelihood of survival of the sample material

<table>
<thead>
<tr>
<th>Site</th>
<th>pH</th>
<th>Eh</th>
<th>Moisture content</th>
<th>Material likely to survive</th>
<th>Material unlikely to survive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alice Holt</td>
<td>Neutral</td>
<td>Slightly reduced</td>
<td>damp</td>
<td>Antler</td>
<td>Horn</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ivory</td>
<td></td>
</tr>
<tr>
<td>Fiskerton</td>
<td>Slightly acidic</td>
<td>Slightly reduced</td>
<td>waterlogged</td>
<td>Horn</td>
<td>Antler</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ivory</td>
</tr>
<tr>
<td>Firestone</td>
<td>Neutral</td>
<td>Moderately reduced</td>
<td>waterlogged</td>
<td>Antler</td>
<td>Horn</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ivory</td>
</tr>
<tr>
<td>Alum Bay</td>
<td>Slightly alkaline</td>
<td>Aerobic/anaerobic</td>
<td>waterlogged/submerged</td>
<td>Antler</td>
<td>Horn</td>
</tr>
</tbody>
</table>

The marine site was not measured but the environmental conditions described are those which might be expected at this type of site. There is a reasonable amount of correlation between the deterioration actually recorded and the deterioration predicted by the burial environments. The marine site does not behave as might have been expected, this may be due to the relatively short burial period and the shallowness of the trench in which the samples were buried.

Protein degradation is a factor in overall deterioration and ranking. This is an example of one component degrading quickly whilst overall weight loss is low, particularly at the marine site. The slightly alkaline aerobic environment causes rapid degradation of
protein due to bacteria and alkaline catalysed hydrolysis but the mineral phase will be protected and slowly replaced by the carbonate in the sea-water.

One of the most interesting factors for conservation is the initial rapidity of the processes of deterioration. There is considerable change even after only three months of burial in all types of material. This would indicate that any recovered materials of horn antler and ivory should be considered to be deteriorated no matter how short the period of burial.

5.3. Developing Models

The development of models to predict the behaviour of materials within monitored environments is theoretically possible provided sufficient data is recorded on the type and quantity of factors controlling the deterioration of materials within the environment. It should be possible to recreate environments within the laboratory and to measure the degradation of different types of sample material which occurs within those environments. Parameters such as pH and Eh, moisture content, salinity and hydraulic conductivity and water levels can all be measured and controlled. The development of laboratory models would be extremely useful for example in assessing the environmental changes caused by sea-level rise and its impact on coastal archaeological sites. If the impact of change could be modelled then this would enable mitigation strategies to be developed and adapted to changing circumstances to protect the cultural resource.

The environmental monitoring data highlights the level of variation between samples over the monitoring period. Whilst the amount of variation has been noted and preliminarily investigated in the results section it has not been mathematically explored.
The differences in values of Eh and pH could be further investigated statistically to explore deviations from mean figures and to assess the significance of some of the results and also to establish whether significant relationships exist between the environmental results and the deterioration recorded on samples.

The variations in degradation between surface and exposed samples and between different burial horizons could be explored further. The relationship between materials as they first become deposited and degradation as they become buried and continue to degrade would be an area which could be investigated both in the external environment and by modelling.

5.4. Consequences for conservation

First Aid or Emergency Conservation is conducted when fragile objects are first excavated to try to ensure that objects remain stable and to ensure their survival (Watkinson, 1987). By controlling the post excavation environment, particularly the levels of moisture, temperature, oxygen, pH and light, rates of deterioration can be seriously reduced. In the past it was difficult to reduce the levels of oxygen in the field therefore conditions were usually controlled by regulating the moisture content of the environment. However recent developments in technology have lead to the development of oxygen scavenging packaging systems which are commercially available and can be used in the field (Graham et al, 2007). These may be useful for the storage of organic materials post excavation to reduce degradation caused by aerobic bacteria and fungi. The area of immediate post excavation treatment and storage is an area which could be useful to investigate further in the future.

The use of freeze drying particularly with material from waterlogged contexts has been undertaken and could be investigated further using various consolidants. This may be
particularly interesting in regard to ivory from waterlogged environments which is a material prone to physical damage caused by shrinkage when it dries (Chadefaux, et al., 2008).

The deterioration of the materials in the burial environment is initially rapid suggesting that the materials will generally be in a fragile condition on excavation. Antler and ivory are composites with an organic component and a mineral component. The nature of deterioration of these materials within the burial environment is broadly that of chemical dissolution, or slow mineral replacement due to cation exchange accompanied by protein degradation caused by hydrolysis and bacterial degradation. On drying the objects may be damaged by salt expansion or general physical disruption caused by shrinkage. Therefore it may prove to be more effective to consolidate these particular materials using a combination of consolidants with bulking agents followed by freeze-drying to reduce drying stresses and shrinkage.

Horn is subject to hydrolysis which is more rapid in alkaline environments. It survives only rarely and is usually in extremely poor condition. Combinations of polymers to act as support and bulking agents may help to support the degraded horn matrix and freeze drying may also be beneficial in reducing drying stresses.

New treatments using naturally occurring polymers such as collagen and keratin could be investigated to assess their potential at repairing the organic phases of the materials. Keratin has recently been used to conserve waterlogged wood (Endo, Kamei, Lida, Yokoyama, Kawahara, 2010), and as these polymers occur within the studied materials it might be appropriate to investigate their use as consolidants. They should be investigated to establish whether they would be effective and to ascertain whether they obeyed the major principles of conservation regarding reversibility and compatibility.
There may be other natural polymers which would be suitable consolidants and there are also alternative bulking agents which could be investigated.

Ivory particularly when recovered from a marine environment is often heavily iron stained. This staining is difficult to remove (Godfrey et al., 2002). Chelating agents have been used in the past to attempt to remove stains but these are harsh and can damage the surface of objects. New methods of removing iron by identifying safe chelating agents or by bioremediation could be investigated.

5.5. Implications of findings for preservation in situ

To increase understanding of the efficacy of in situ preservation, there must be an agreement of what the term actually means (Van de Noort et al., 2001). The term preservation in situ has been used as a catch all phrase to describe various situations which it may now be useful to differentiate.

1. Re-watering. This involves the rewatering of an entire site or landscape containing archaeological remains to ensure its long-term preservation. This has been undertaken at a number of sites containing organic archaeological remains where the drying out of the landscape has threatened to dessicate the environment. These activities have been undertaken at locations such as Sutton Common (Parker Pearson, M. and Merrony, C. 1993), the Sweet track in Somerset (Brunning, R. 1999) and at one of the sites used in this study Fiskerton in Lincolnshire. At Fiskerton this involved blocking drainage ditches to allow water levels to rise and cover the organic archaeological remains to a depth at which they would be preserved. These changes would appear to be succeeding in their aims with the environmental data indicating that the site has become more passive. In general the rewatering of sites or landscapes tends to be on a large scale and
affects archaeological areas which have been sampled or partially excavated but not fully excavated.

2. **Reburial of an excavated site.** The reburial of sites which have been excavated and then covered to preserve them post excavation. Generally artefacts are excavated and removed from the site but structural remains have been covered to protect them *in situ.* Other examples include the excavation and recording of large objects such as log boats or shipwrecks which are excavated recorded and then preserved *in situ* by reburial. The first managed and monitored reburial in England took place at the Rose Theatre in London. Here an Elizabethan theatre was discovered and preserved *in situ.* A burial methodology was devised and implemented and a monitoring regime undertaken (Corfield, 2004).

3. **Natural Storage.** This term can be used to describe the process of reburying excavated archaeological artefacts in an environment which could be considered conducive to its survival. There are examples where waterlogged wood for example has been excavated and reburied at a site different from the site where it was excavated (Gregory, D. 1999). Waterlogged wood has been excavated stored, recorded and moved to wetland sites which have been identified as providing conditions which would ensure their preservation. Firestone Copse a site used in the study is a site which has been identified as having the potential to be used for this type of reburial (Hogan, *et al.* 2006). The site at Alice Holt was relatively protective at greater depth suggesting that damp clays are potentially good preservers of certain types of material. The crucial factor is the maintenance of saturation and the creation of anaerobic conditions to prevent microbial degradation and hydrolysis of minerals.

Preservation *in situ* may in some cases be desirable and in some cases may be the only option available for the preservation of archaeological remains. It is however important
to differentiate the environmental requirements of the types of material to be preserved and to ensure that the environmental conditions are suitable for the preservation of those particular materials. Large quantities of roof tiles may be stored perfectly safely in a terrestrial environment in a trench lined with geotextile and filled with inert sand, walls can be protected by a similar form of reburial. Some waterlogged archaeological materials such as wood can be stored in nature for long periods of time providing that suitable environmental conditions can be identified, monitored and maintained.

The materials used in this particular study are not necessarily suitable candidates for reburial leading to preservation in situ. This does not mean however that in certain circumstances they will not be preserved. Mammoth ivory is relatively commonly preserved in waterlogged anaerobic environments for tens of thousands of years (Turner-Walker, 1998). Similarly antler given suitable conditions can be preserved (Chadefaux, et al. 2008). However the material which survives will be much changed from the material which initially found its way into the burial environment. Horn is rarely found on excavations, it is subject to degradation by microorganisms and to hydrolysis which means that it is difficult to find a burial environment in which it can survive in the long term.

If in situ preservation is to be carried out the depth of reburial should be at least 50 cm on both marine and estuarine sites. Suggestions for methods of reburying artefacts are set out below in Fig. 5.1.
**Fig. 5.1** Models for carrying out in-situ preservation at marine and estuarine reburial sites

<table>
<thead>
<tr>
<th>Marine (model)</th>
<th>Estuarine (model)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seawater</td>
<td>Topsoil</td>
</tr>
<tr>
<td>50cm Sand</td>
<td>50 cm Estuarine silt</td>
</tr>
<tr>
<td>Layer of sandbags</td>
<td>Artefacts</td>
</tr>
<tr>
<td>Sediment Terram 4000</td>
<td></td>
</tr>
<tr>
<td>Artefacts</td>
<td></td>
</tr>
</tbody>
</table>
5.6 Conclusions

- The literature suggested that these materials were poorly understood and that the methods of treating them after excavation were inadequate. By investigating and developing a greater understanding of the degradation of the materials within the environment suggestions for new methods of conservation treatment could be devised.

- The development of methodologies for environmental monitoring produced standardised data which can be used to compare different burial sites. This data can be used in the construction of biogeochemical models to study the impact of environmental change on archaeological sites and materials.

- At the marine site the slightly alkaline aerobic environment causes rapid degradation of protein by bacteria and alkaline catalysed hydrolysis but the mineral phase will be protected by the sea-water leading to the survival of antler and ivory but the rapid degradation of horn. However although antler and ivory may be preserved in these environment they will also be changed by it. The burial site at Firestone proved to be the most protective for antler and ivory, the combination of a reduced waterlogged environment with brackish water and fine estuarine silt is conducive to the preservation of organic materials. The potential for estuaries as sites for the in situ preservation of organic materials should be investigated further.
• One of the most interesting factors for conservation is the initial rapidity of the processes of deterioration. There is considerable change even after only three months of burial in all of the types of material studied. This would indicate that any recovered materials of horn antler and ivory should be considered to be deteriorated no matter how short the period of burial.

• Microorganisms were visible on some SEM images of the recovered samples. The ability of collagenase to alter powdered ivory and powdered red deer antler was also demonstrated.

• Horn is an unsuitable material for passive conservation methods. It will continue to deteriorate unless it is properly conserved.

• The use of a number of different analytical techniques to analyse the samples was useful in that it highlighted a number of processes that would have been missed using fewer techniques. FTIR and weight loss are particularly useful for all of the materials with XRD being less so.

• XRD and FTIR would be useful techniques for examining antler and ivory which had been buried for greater periods of time. The combination of the two techniques would provide data regarding protein degradation and establish if changes were taking place in the mineral structure after long periods of burial.

• The ability to interpolate the amount of deterioration of samples over time can be achieved by using weight loss. Weight loss could be used to predict the deterioration of materials over time if the burial periods were longer.

• A combination of polymers to act and bulking agents may help to support the degraded horn matrix and freeze drying may also be beneficial in reducing drying stresses. A similar approach should be used for ivory and antler with
polymers used to reintroduce elasticity, bulking agents to fill cavities and 
freeze-drying to reduce drying stresses.

- The construction of biogeochemical models to study the impact of 
environmental change on archaeological sites and materials would be possible 
by devising laboratory experiments which mimic the burial environment and 
where environmental conditions can be altered to simulate changes. Organic 
materials could be seeded within these environments and monitored to assess 
how they perform in varied environmental conditions.

- FTIR studies should focus on the deterioration of protein within specific Amide 
I and Amide II bands. The peaks within the bands should be identified to 
ensure that the monitoring of deterioration can be focussed on areas where 
deterioration is taking place.

- Biological evaluation suggested that deterioration by collagen degrading 
bacteria was likely within the samples. Future work should concentrate on the 
identification of organisms using molecular techniques and on the study of horn 
to establish the nature of protein degradation and to establish if fungi are 
playing a role in its deterioration.

- New materials for First Aid, cleaning and interventive conservation treatments 
should be investigated.
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## APPENDIX A

**ENVIRONMENTAL MONITORING: TABLES OF RESULTS**

*Table A.1* Mean, maximum and minimum recorded levels of Eh potential at the monitored sites.

<table>
<thead>
<tr>
<th>Site</th>
<th>Sample</th>
<th>Min</th>
<th>Mean</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terrestrial (Alice Holt)</td>
<td>1</td>
<td>N/D</td>
<td>N/D</td>
<td>N/D</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>N/D</td>
<td>152</td>
<td>N/D</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>23</td>
<td>135</td>
<td>184</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>36</td>
<td>125</td>
<td>195</td>
</tr>
<tr>
<td>Freshwater wetland (Fiskerton)</td>
<td>A</td>
<td>-199</td>
<td>-35.71</td>
<td>161</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>-133</td>
<td>-5</td>
<td>159</td>
</tr>
<tr>
<td>Brackish wetland (Firestone Copse)</td>
<td>50</td>
<td>-166</td>
<td>-64</td>
<td>182</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>-207</td>
<td>-91</td>
<td>148</td>
</tr>
</tbody>
</table>
### Table A.2 Mean, maximum and minimum recorded levels of pH at the monitored sites.

<table>
<thead>
<tr>
<th>Site</th>
<th>Sample</th>
<th>Min</th>
<th>Mean</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terrestrial (Alice Holt)</td>
<td>1</td>
<td>N/D</td>
<td>6.9</td>
<td>N/D</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>7.5</td>
<td>7.59</td>
<td>7.7</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>6.52</td>
<td>7.02</td>
<td>7.8</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>6.18</td>
<td>6.85</td>
<td>8.16</td>
</tr>
<tr>
<td>Freshwater wetland (Fiskerton)</td>
<td>A</td>
<td>6.09</td>
<td>6.63</td>
<td>7.74</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>6.05</td>
<td>6.46</td>
<td>6.46</td>
</tr>
<tr>
<td>Brackish wetland (Firestone Copse)</td>
<td>50</td>
<td>5.23</td>
<td>6.62</td>
<td>7.62</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>4.96</td>
<td>6.96</td>
<td>7.84</td>
</tr>
</tbody>
</table>

### Table A.3 Combined table illustrating the maximum, mean and minimum levels of Eh and pH at the monitored reburial sites.

<table>
<thead>
<tr>
<th>Site</th>
<th>Sample</th>
<th>Min Eh</th>
<th>Mean Eh</th>
<th>Max Eh</th>
<th>Min pH</th>
<th>Mean pH</th>
<th>Max pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terrestrial</td>
<td>6</td>
<td>36</td>
<td>125</td>
<td>195</td>
<td>6.18</td>
<td>6.85</td>
<td>8.16</td>
</tr>
<tr>
<td>Freshwater wetland</td>
<td>B</td>
<td>-133</td>
<td>-5</td>
<td>159</td>
<td>6.05</td>
<td>6.46</td>
<td>8.61</td>
</tr>
<tr>
<td>Brackish wetland</td>
<td>100</td>
<td>-207</td>
<td>-91</td>
<td>148</td>
<td>4.96</td>
<td>6.96</td>
<td>7.84</td>
</tr>
</tbody>
</table>

### Table A.4 Conductivity levels species recorded from the three monitored burial sites.
<table>
<thead>
<tr>
<th>Site</th>
<th>Sample</th>
<th>Conductivity (μS cm(^{-1}))</th>
<th>Min</th>
<th>Mean</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>freshwater wetland (Fiskerton)</td>
<td>Piezometer 2</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
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**Table A.5** Iron levels recorded from the three monitored burial sites.

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<th>Site</th>
<th>Sample</th>
<th>Iron Mg/L</th>
<th>Min</th>
<th>Mean</th>
<th>Max</th>
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</thead>
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<td>B</td>
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<tr>
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**Table A.6** Sulfate levels recorded from the three monitored burial sites.
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<td>Mean</td>
<td>Max</td>
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<tr>
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**Table A.7 Chloride levels recorded from the three monitored burial sites.**

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<td>Mean</td>
<td>Max</td>
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**Table A.8 Sodium levels recorded from the three monitored burial sites.**
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<td>N/D</td>
<td>N/D</td>
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<td></td>
<td>B</td>
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