marine cast iron, where the temperature required can be reduced to 850 or 600°C by heating in a reducing atmosphere of hydrogen, or even 400°C by heating for long periods of time.[46] The cast iron is not only stripped of chloride ions, it is also strengthened and made to appear more like the original material by the reduction of iron oxide in the graphitized zone (section 5.2.2.3) to metallic iron and magnetite. There is, however, some alteration in the metallurgical structure of any original iron at these high temperatures. It may be considered that this loss of information is permissible in return for the success in the stabilization of marine cast iron, which is extremely difficult to achieve by any other method. Controversy[47] has arisen when this treatment has been applied to ancient steel and wrought iron which, as shown in section 5.2.1, in all likelihood will also contain carbon. A great deal of metallurgical detail will be lost if these materials are heated over 380°C. Moreover, if reduction takes place at these lower temperatures, it is unlikely that all the chloride will be driven off. Compared with other methods of chloride removal, hydrogen reduction is relatively quick, but this alone cannot outweigh the drawbacks in its use on low-carbon alloys.

Thus at present there are no wholly satisfactory methods for the reduction in chloride levels in excavated ironwork available, and in most cases passive stabilization techniques for chloride-laden iron are to be preferred until reliable methods of active stabilization have been developed and tested.

Having reduced the chloride levels, it is essential to remove as much water as possible from ironwork; this is best achieved using displacement by solvents rather than heat (see above). It is then usual to put a film over the surface of the object to prevent recontamination by chlorides, dust pick-up, and wear and tear during handling. The incorporation of pigments or graphite into the wax or lacquer applied is neither useful nor, since it obscures the surface, in the interests of future examination. On the rare occasions in archaeological material where the surface of the object is of metallic iron, a protective chemical coating in the form of tannins or phosphates (section 5.2.2.1), or even paint, could be applied where the object unavoidably is to be exposed to harsh climatic conditions. However, since these alter the colour of the iron and mask details, and are not enduring nor reliable, it is more advisable to remove the object to an environment which can be controlled.

After chemical stabilization, consolidation of fragile artefacts using synthetic materials (section 3.4.2.2) may be necessary, but resort to embedding in a transparent block of resin, as has been suggested, should be avoided for obvious reasons.

5.2.6.3 Long-term environmental control

To consider this, ironwork must be divided into two types, namely that which is found to be stable or has been actively stabilized and that which is only stable by means of passive control of the environment. If ironwork falls into this latter category, then long-term stabilization simply consists of an indefinite continuation of the techniques described in section 5.2.6.1. It is known that at least some iron excavated from land sites will withstand up to ten years' storage in desiccated environments, but lengthy wet storage is likely to prove less satisfactory.

Alternatively, if ironwork falls into the first category, whilst less stringent conditions of RH control are required, it has to be treated as a sensitive material. This means that neither temperature nor RH can be allowed to fluctuate greatly. To prevent the advent of corrosion of any remaining metal, the RH is kept below 65 per cent, metallic surfaces are handled only with gloves, and dust is prevented from settling on the objects. As for all other artefacts, gross pollution is destructive; in extreme cases of atmospheric pollution by sulphur dioxide or salt spray, corrosion can be prevented only by maintaining a very low RH. Vapour phase inhibitors (section 5.1.5) might be used in an enclosed container but some of these suitable for iron actually cause copper to corrode and so must be used advisedly.

5.2.7 Summary

Ironwork, especially wrought iron and artefacts from the sea, is perhaps the most problematic, in terms of both investigative cleaning and stabilization, of all material excavated. Research being carried out will, it is hoped, point to means of developing more satisfactory conservation techniques than are available at present.

On site, the only treatment given to iron should be that of careful handling and passive stabilization, and this should begin as soon as possible after exposure. Since the technique of stabilizing ironwork from land sites varies between conservation laboratories, it is essential that liaison with the laboratory which is to treat the iron is established before excavation, to determine the method of passive stabilization required. Where there has been a failure to liaise with a laboratory before excavation, an indefinite delay in the treatment of the material is likely; in this case it is suggested that the ironwork be desiccated (section 3.4.1.1), a process which should begin within forty-eight hours of exposure. The opposite is correct for marine ironwork: it must be kept wet (section 5.2.6.1) from the moment of removal from the sea. Again, advice is essential.

Adequate publication of ironwork cannot take place without radio-

graphy; without this, much evidence is missed or misinterpreted. Investigative cleaning, likewise, is essential for competent assessment of a site and cannot be performed without the use of radiographs. Illustration of ironwork should be carried out with reference both to the artefact and to its radiograph: if the artefact is used alone, corrosion crusts may be misinterpreted; and if radiographs are used alone, distortion occurs and a third dimension of morphology is lost. It cannot be said too often that for publication and display of ironwork liaison between excavator, conservator, and curator is essential.

In the absence of satisfactory methods of active stabilization of iron, control of the storage and display environment is indispensable. As ironwork is a sensitive material, its condition has to be monitored regularly and indefinitely.

5.3   Lead and its alloys

5.3.1   Nature of artefacts

Pure lead has a low melting point of 327°C and since its recrystallization temperature (section 5.1.1) is below normal, ambient, room temperature it does not respond to work hardening. Soft lead is not suitable for thin-walled hollow vessels etc., and for these and other cast objects, harder and stronger alloys are used. Such an alloy is pewter but, being in the main tin, it is dealt with in section 5.4. Silver is often present in lead objects in small percentages since the metals have a common ore type; both this and cold working increase the corrosion resistance of a lead artefact. Also common in low-grade lead may be impurities such as chlorides and sulphur. Joins in leaden objects can be made either by cold welding or by soft soldering (section 5.1.2.1) and the relative softness of the metal and even of pewter means that it can be readily inscribed or stamped.

5.3.2   Nature of deteriorated material

5.3.2.1   Appearance

DULLED OR SHINY BROWN SURFACE. In the atmosphere, a thin layer of lead oxide (PbO) will form a protective layer over the metal; sometimes this layer may contain darker lead sulphides as well.
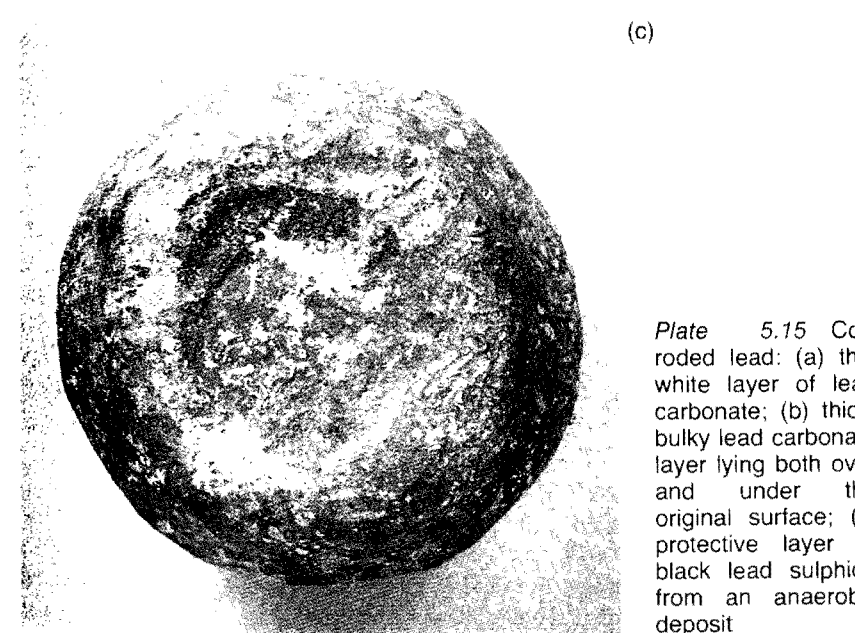
THIN WHITE/DISCOLOURED LAYER (plate 5.15a). This is normally cerussite, lead carbonate ($PbCO_3$) and/or hydrocerussite, basic lead carbonate ($2PbCO_3.Pb(OH)_2$), which, having been formed slowly in the presence of air and water, have protective structures made of compact adhering

(a)
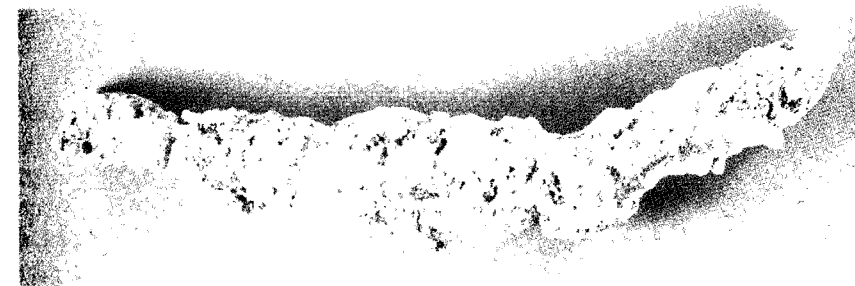
(b)

(c)

Plate   5.15 Corroded lead: (a) thin white layer of lead carbonate; (b) thick, bulky lead carbonate layer lying both over and under the original surface; (c) protective layer of black lead sulphide from an anaerobic deposit

crystals. They are found on lead from damp, calcareous soils and also on lead from the sea and in both cases protect the metal from greater corrosion. This layer may include the white lead sulphates, anglesite, and leadhillite and be contaminated with phosgenite ($PbCl_2.PbCO_3$) and other chlorides in the sea.

WHITE OR DISCOLOURED CRUST (plate 5.15b). Again this crust is mainly cerussite or hydrocerussite but it can be discoloured by oxides; pink/red/brown litharge (αPbO), yellow massicot (βPbO) or brown plattnerite (PbO_2). It may be tinged grey, by black galena (PbS), and become fissured horizontally and vertically, the crevices becoming filled by soil and roots. Corrosion forming these crusts occurs only in alkaline soils since the carbonates dissolve in acidic pH. In alkaline soils where carbonates are sparse, lead appears to corrode to reddish brown oxides with little if any carbonate; specks of lead metal may remain in this crazed and fissured crust.

BLACK OR DULL GOLD COLOUR LEAD (plate 5.15c). From anaerobic environments, whether marine or terrestrial, containing active sulphate-reducing bacteria (section 2.1.1.2), lead is blackened with lead sulphide, galena (PbS). This may be an adhering protective coat or just a sludge with no lead remaining. Occasionally lead from such deposits may appear dull gold in colour: this may result from deposition of copper and iron sulphides.[48]

OVERLYING ENCRUSTATIONS. In conditions where lead is well preserved (section 5.3.2.2), overlying concretions of calcium carbonate (calcite and aragonite) are found: in sea-water these are accompanied by barnacles.

5.3.2.2 Implications of corrosion

In the presence of air, water, *and* organic acids, lead corrodes extremely quickly since the primary corrosion products of organic salts, such as acetates and formates, are all soluble (figure 5.7). Similar rapid corrosion occurs in soft, acidic waters when no protective carbonate layers form.[49] If such conditions prevailed in a deposit, it is unlikely that lead would survive more than half a century of burial. At the other extreme, lead is extremely resistant to corrosion by sea-water and chalky soils. Topographical details of the original surface are often maintained by the outer surface of a corrosion film or crust. However, sometimes the crust is distorted and the only detail remains in an underlying metal core where this does survive. Such remaining metal will be much pitted and only retain diminished details. It would seem that, unlike iron, there is no level of an 'original' surface to be found within a distorted lead corrosion
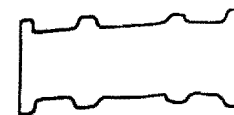
1. Well preserved covered by thin film of corrosion products
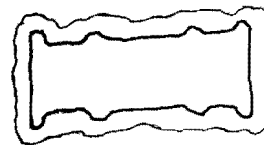
2. Original surface retained by metal surface which is slightly eroded: covered in layer of corrosion products or concretions of varying thickness
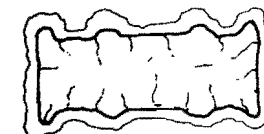
3. Original surface retained by exposed surface of corrosion products: remaining metal (if any) bisected by cracks.

Figure 5.7 Common conditions of lead found on excavations; cross-section of a token

crust. Corrosion can penetrate deep into lead, down grain boundaries, and thus it is much more brittle than it appears.

5.3.3 Examination

Some notion of the amount of lead in an alloy can be estimated simply by weight, but where bright metal is exposed it is found that lead will mark paper but tin and fine pewter will not. Since topographical details such as incised markings or stamps or an original surface are often maintained by the surface of a corrosion layer or crust, maximum information about a lead object can often be gained without having to remove corrosion products. Corroded lead can be very brittle since corrosion may have penetrated deep into it; care is taken to distinguish between corrosion products and earth/rootlets within the crevices of a crust. If much lead metal remains, x-radiography is of little help since this material absorbs x-rays, preventing exposure of the underlying film. In exceptional cases, neutron radiography (section 3.3.1.3) would be used.

5.3.4 Cleaning

5.3.4.1 Cleaning of lead from land sites

Investigative cleaning of this material usually consists of careful manual removal of overlying soil and concretions without dislodging the corrosion crusts or material within the crevices holding it together.

Plate 5.16 Stripping corroded lead. (a) A medieval badge as excavated showing obscuring concretions overlying a well preserved lead surface. (b) The badge after stripping reveals details of the original surface retained in the metal which is pitted by corrosion

Where the crust is distorted *and* examination shows that a good core of metal remains, for examination and display it may be necessary to strip the object (plate 5.16). This type of cleaning is normally carried out electrolytically[50] (section 5.1.4.2), for several reasons. First, since most of the corrosion products of lead are very insoluble, any reagent which will dissolve the crust tends to attack the lead too. This problem extends to the use of the sequestering agent (section 3.3.2.1) disodium EDTA.[51] for if traces of this are left behind after treatment long-term deterioration due to organic acids (section 5.3.2.2) may occur. Second, mechanical cleaning may smear or scratch the very soft metal underlying a lead corrosion crust. Third, there is no 'original' surface to locate within the crust mechanically. Furthermore, since lead and its corrosion products are poisonous, the dust produced by mechanical cleaning is toxic. On occasions, objects require this 'stripping' treatment only in discrete areas: here local electrolysis (section 5.1.4.2) using a pencil as an anode is used.

5.3.4.2 Cleaning of marine lead

It is not usually necessary to clean marine lead because surface encrustations are rarely obscuring. Occasionally, however, lead ingots or the stocks of Roman anchors may have identification marks which are disfigured by corrosion crusts. In this case, mechanical removal to reveal the blurred metal may be undertaken with wooden tools which minimize the risk of damaging the lead. Such cleaning is kept to a minimum and only carried out when the information possibly to be gained is essential to the dating or identification of the wreck or artefact, for it may result in damage without the benefit of information revealed. The mechanical removal of small patches of tightly adherent carbonate deposits from lead which is otherwise uncorroded can cause damage, but so also will almost any chemical used to dissolve the carbonate. Oddly, dilute sulphuric acid, subsequently neutralized, is the least damaging as it reacts to form an insoluble but often visible layer of lead sulphate on the surface of the etched metal, preventing further attack.

5.3.5 *Deterioration of lead alloys after excavation*

Lead alloys and their corrosion crusts after excavation are normally chemically stable, unless they become contaminated by organic acids either from injudicious conservation treatments or injudicious storage. Sources of these acids are certain waxes, lacquers, cleaning chemicals, papers, cardboard, cotton wool, woods (especially oak), paints, fabric finishes, and adhesives. With only slight moisture, these acids cause the corrosion described in section 5.3.2.2. Since the organic lead salts are not washed away, they react further turning the lead within a matter of months into soft white carbonate which crumbles on touching (plate

5.17a). Lead containing chloride and sulphur impurities may react with oxygen and moisture disrupting an already decayed object.[52]

Normally lead corrosion crusts containing details of an original surface (section 5.3.3) are not physically robust and can be destroyed by mishandling. Furthermore, if corrosion crusts are held together by soil in crevices, drying out after excavation may lead to crumbling. Even a relatively low level of heat, such as that from a light, can cause leaden artefacts to sag and become distorted.

5.3.6 Stabilization

5.3.6.1 Passive

Stabilization of lead is mainly confined to the avoidance of heat, mishandling, and contamination by organic acids. This latter condition is achieved by storing the artefacts, once dry, in sealed polypropylene boxes which do *not* contain materials which give off organic acid vapours; to be avoided are crude papers, cardboards, and cotton wool etc. Alternatively, objects can be placed inside acid-free paper envelopes which have been impregnated with calcium carbonate to absorb any such vapour. When on display, again lead must not be allowed to become contaminated; in these situations sources of organic acid include oak cabinets, paint, and cloth. Testing materials suspected of giving off organic vapours has been mentioned earlier (section 3.4.1.5).

Where it is found that lead has been contaminated or contains chloride and sulphur impurities, decay may be slowed down by desiccating it to an extremely low RH with silica gel; long-term stabilization is achieved only by an active technique described below.

5.3.6.2 Active

Crumbling carbonate crusts may be consolidated only with resins which do not contain nor break down to form organic acids; many waxes, PVAC, etc., are thus excluded. A technique called 'consolidative reduction' has been devised to reduce lead carbonate to lead making a much corroded object stronger and more visually attractive.[50] Unlike when reducing corroded iron (section 5.2.6.2) or lead ore, heat and a reducing atmosphere are not used; instead a very low electric current is applied whose direction is the exact opposite of the corrosion current (section 5.1.3.2). Electrons are taken up by the lead ions, reducing them to lead. It is a tricky procedure and carries with it ethical considerations (section 3.4.2.3). But since this technique alone also removes organic acids from a crumbling contaminated crust, it has to be employed to stabilize this type of material (plate 5.17b).
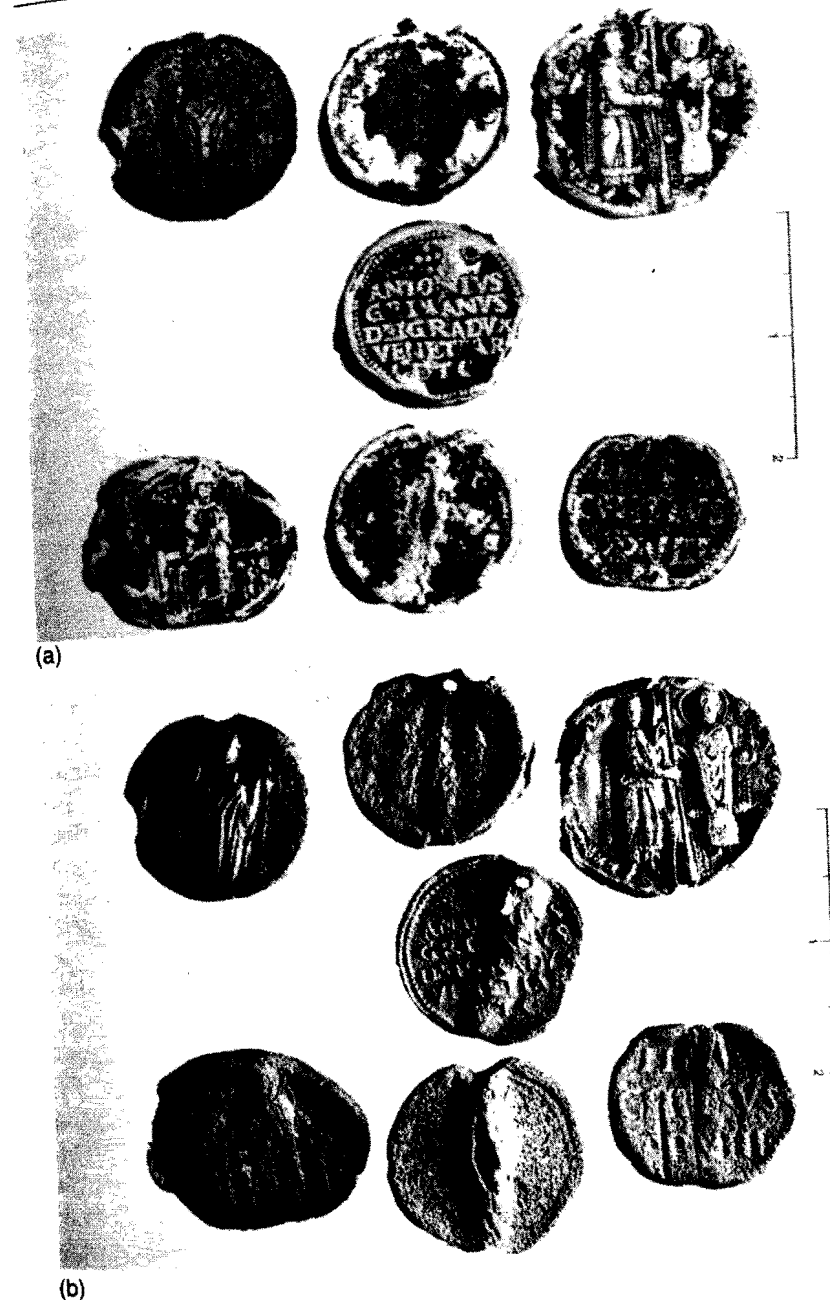
(a)

(b)

Plate 5.17 (a) Lead seals, corroded in store to soft, white lead carbonate, have survived only because the powder is held together by an old blackened wax coating. (b) Same seals after the lead carbonate has been electrolytically reduced back to lead

It is usual to prevent surface contamination and corrosion of clean lead by the application of a coat of synthetic resin, but as with consolidants the choice is restricted to those which are free from organic acids.[50]

5.3.7 Reshaping

Although lead can be worked without the need for annealing, reshaping is a specialist technique. Lead which appears sound may have corrosion penetrating deep into it (section 5.3.3), introducing brittleness into the material and thus precluding reshaping without the danger of cracking. Moreover, any corrosion crust containing surface detail such as lettering could crumble or become abraded in the process.

5.3.8 Summary

Objects made of lead or its alloys cannot be cleaned or reshaped without damage except under laboratory conditions. On the whole, excavated material does not require extensive environmental control, careful handling and avoidance of heat perhaps being most essential. Where the lead is thought or feared to be low grade, it should be desiccated (section 3.4.1.1). In the longer term, however, the role of organic acids as corrosion stimulators becomes important and thus care has to be taken to avoid excavated material becoming contaminated by organic acid vapours or solutions. Once contaminated, there exists only the one rather drastic recourse of consolidative reduction for stabilization. Cleaning of lead likewise does not usually entail extensive work; virtually all detail that can be seen on excavation is all that there is preserved.

5.4 Tin and its alloys

5.4.1 Nature of artefacts

Tin has a very low melting point (232°C) and good wetting power, and so is often used for casting or as a coating. However, cast tin objects are soft and so it is usually alloyed for strength as well as economy, giving pewter.[53] This term covers a wide range of mainly casting alloys from 25–50 per cent lead (Roman), to less than 25 per cent lead ('lay' medieval), to tin with a small amount of copper, bismuth, or antimony ('fine' medieval and modern). An alloy with more than 25 per cent lead must be considered poisonous. Coatings of tin alloys are generally referred to as 'tinning', and whilst they could be of almost pure tin, they are more likely to be low-melting-point tin alloys; the alloying material is lead, but antimony, copper, and zinc are also possible. Since tin/lead and

lead/tin alloys have such low melting points, that of 63 per cent tin being 183°C, they are used frequently as soft solders (section 5.1.2.1).

5.4.2 Nature of deteriorated material

BRIGHT TIN OR PATINATED PEWTER. Though a base metal, tin and tinning often present a bright surface even after many years, as a result of the formation of a thin film of protective tin(IV) oxide (SnO_2) which is resistant even to acid attack. This oxide layer helps preserve tin even when it should be forming the anode in a galvanic cell (section 5.1.3.2), as it is when being used to coat copper alloys. When combined with lead oxide and possibly sulphide, tin oxide gives pewter, especially from the sea, a fine grey patina.

BLACK SPOTS, PITS, OR WARTS. If a damp environment contains corrosion stimulators such as chlorides or sulphates, localized roughening of the surface appearing as black spots occurs.[54] If corrosion continues, pits are formed. Alternatively, cassiterite (SnO_2) is found and appears as hard warts.

GREY/WHITE/BROWN CRUST. Continued corrosion caused by stimulators can produce a crust usually of SnO_2 with some tin(II) oxide. Black romarchite (SnO) and white hydroromarchite ($5SnO.2H_2O$) have been identified on tin from fresh water.[55] These crusts may be discoloured by other metals present, copper for example, turning them green, or they may be dissected by crevices. Crusts on alloys with lead, will also contain lead corrosion products (section 5.3.2.1); pewter from marine sites may appear with a soft grey surface sprinkled with warts as above. That pewter sometimes appears disfigured and sometimes with a preserving patina, seems to depend more on the proportion of lead in the alloy than on any recognizable feature of the environment. In extreme conditions, crusts may crack, curl up, and spall off.

GREY/WHITE/BROWN POWDER OR PASTE. Corrosion may continue right through an object or solder, reducing them to powder which normally crumbles away. On occasion it may be held together fortuitously by other salts, such as silicates, from the soil, in which case it may be difficult to recognize the object as having been originally metallic.

There are few examples of tin from marine environments, probably because here its main corrosion product, tin oxide (SnO_2) forms white paste-like deposits. These usually only survive when they are protected by marine sediment or concretion. Romarchite (SnO) and yellow varlamoffite ($(Sn.Fe)(O.OH)_2$) also form in marine environments, but so far have

only been recorded in association with corroded bronze and brass. Hydrated chlorides have also been found.

ISOLATED PITS CONTAINING GREY POWDER. This type of decay is seen only rarely and should not be confused with those described above. It can occur only where the temperature is less than 13°C, when the crystal structure of the tin is altered in discrete areas, turning the bright metal to a grey powder called 'tin pest'. The reason for this alteration is still unclear, but the possibility that much buried tin has been lost through long exposure to temperatures below 13°C is not credited by some metallurgists.[56]

5.4.3 Examination

If an object of tin or pewter just has a thin oxide film, the original surface topography and dimensions will be well maintained. If the film's crust and corrosion is extreme, neither any remaining metal core nor any corrosion layer within the crust retains details of the original surface; the outside surface of the corrosion products must be used as a guide to the original. Fortunately, the volume expansion of the corrosion crust is not normally excessive.

On objects made of metals other than tin, any 'tinning' present may not be visible; being less base than iron and being protected by its oxide film (section 5.3.2.1), tinning can become covered by iron or copper corrosion products. X-radiography assists in this search, but it often fails to detect thin coatings. Solder also should be looked for, but, being rich in lead, it is often corroded to powder when in contact with copper alloys.

5.4.4 Cleaning[57]

As with lead alloys (section 5.3.4), little cleaning, apart from dirt removal, is carried out. Warts of tin oxide are not removed, as corrosion of the exposed metal is liable to occur very quickly. If, for some reason, removal of cassiterite is required, it would be extremely difficult to carry out chemically since this is so insoluble. Patinas on pewter are prized and should always be retained.

5.4.5 Deterioration after excavation and stabilization

After excavation, tin alloys usually are found to be chemically stable, either because they are preserved by a layer of oxide, or because no metal remains. Occurrences of tin pest (section 5.4.2) have been found on historic tin, but the extent of this type of decay is not known. At present, tin alloys are stabilized only passively, by maintaining the temperature

above 13°C, whilst bearing in mind the low melting point of tin. Pewter, like lead (section 5.3.6.1), must be protected from organic acids.

5.4.6 Summary

As for lead (section 5.3.8).

5.5 Copper and its alloys

5.5.1 Nature of artefacts[58]

The melting point of pinkish copper (1084°C) is reduced by small quantities of natural impurities such as arsenic, antimony, tin, lead, or iron. Arsenical copper is more easily work hardened than pure copper, but if present in concentrations greater than 2.5 per cent, the arsenic may cause embrittlement and if greater than 15 per cent, it may rise to the surface of the alloy when cast, giving it a 'silver' skin. Where tin is present in concentrations greater than 2 per cent, it may be considered deliberate alloying to produce bronze, which is harder than pure copper, even without working. A common alloy mixture of 10 per cent tin is a reddish yellow and is readily cold worked; at 14 per cent, a brittle phase makes the now golden bronze harder but more difficult to work; at over 20 per cent, the virtually unworkable bell-metal bronze looks paler; at above 30 per cent, tin may separate out in casting to give a white surface layer or form the brittle high-tin bronze, speculum, used for mirrors etc. To improve casting properties, lead is added to bronze. Alternatively a ternary alloy composed of copper, tin, and zinc (the latter resulting in a paler metal) has increased malleability. This alloy is nearer in character to the modern alloy 'gun metal' than to bronze. Copper alloyed with zinc on its own at about 20 per cent gives golden brasses, whilst higher concentrations give whiter alloys. Since it is impossible to gauge the exact make-up of copper alloys without analysis, in the absence of this it is essential that the alloys are referred to by the generic name of 'copper alloy' rather than by a specific, unproven, prejudicial term such as 'bronze'.

Copper alloys can be joined (section 5.1.2.1) by hard solders, this being known as brazing. The solder itself is frequently a copper alloy; thus a high-tin bronze can be used to braze a low-tin bronze. Brazing solders (or spelters) of copper alloys, especially brass, are used to braze iron as well. Alternatively, weaker joins in a copper alloy artefact can be made with soft solders.

Parts of copper alloy objects can be joined together other than mechanically or with solders, by burning or running on, that is the casting of part of an object directly onto a previously formed piece. However,