DETERMINING THE STABILITY AND DURABILITY OF ARCHAEOLOGICAL MATERIALS

David Thickett[1], Sarah Lambarth[1], Paul Wyeth[2]

[1]English Heritage, 1 Waterhouse Square, 138 Holborn, London EC1 2ST, UK,
david.thickett@english-heritage.org.uk +44 (0)207 973 3322

[2]Textile Conservation Centre, University of Southampton Winchester Campus
Park Avenue, Winchester, SO23 8DL, UK

ABSTRACT

The heavy alteration of archaeological materials makes them environmentally sensitive and, amongst the most challenging, to safely display and store. Non-destructive testing can provide vital information to inform preventive conservation decisions, ensuring the continued preservation of this sensitive material.

The heavy chloride contamination of archaeological metals makes some artefacts extremely vulnerable to ambient relative humidities. Copper alloy objects can corrode at RHs above 42%, whilst some archaeological iron can rapidly deteriorate at RHs above only 19%. Composite objects with organic components, that will be damaged by low RHs, present a particular challenge. Displays often contain mixed media, and balancing environmental needs between organic artefacts and metals that require low RHs is extremely difficult. A certain proportion of archaeological copper and iron alloys have much lower chloride levels and are relatively stable. Completely mineralised iron artefacts are no longer highly reactive. The challenge is to determine the unstable material within an archaeological metal collection.

Radiography, with image processing to identify pits within archaeological iron, has been used to determine the most vulnerable material. Oxygen consumption measurements have been applied to both iron and copper alloy artefacts to measure and predict their reactivity. These analyses have allowed non-reactive material to be displayed safely without environmental control, maximising resources towards the vulnerable material and eliminating the risk to associated artefacts.

Architectural stone is expensive to store. A program of reburial on the original sites of durable, low research potential stone has been initiated. Portable x-ray fluorescence and near infra-red spectroscopy has been utilised to identify sandstones and preclude calcite or iron bound sandstones that would be at risk from burial. These techniques are being used, amongst others, to compare the deterioration rates of sandstones in stores and buried.

INTRODUCTION

Reaction between archaeological metals and chloride ions during burial can render them extremely unstable at ambient relative humidities (RHs). A recent audit of English Heritage's 500,000 archaeological artefacts determined that iron artefacts had undergone the highest level of damage of any material [1]. Whilst dry storage or display will arrest this decay and methods have been developed to achieve this reliably, they require significant resources to set up and maintain [2,3]. Mixed display is also a serious issue, with rigid organic materials undergoing physical deformation and damage at low RHs. Whilst the 35% RH required to retard bronze disease can be tolerated by most organic materials, the 20% required for archaeological iron artefacts, poses a serious risk of damage. This situation is most acute for mixed organic/metal artefacts. Table 1 shows the proposed showcase contents for a new presentation project at Lullingstone Roman Villa, Kent, United Kindgom. Almost one third of the cases require compromise environments because of their mixed contents.

1

Case \ RH	ceramic	stone	copper alloy	iron	lead	silver	bone	leather	glass	mixed objects
	-	-	<42	<30	<40	-	35-65	40-60	35-65	
1	1									
2				1						
3	8	2		6						
4	23			1						
5			12	11						
6	2			1	1		8			bone & iron
7	2	4	1				9			bone & iron
8							2		2	
9						2				
10				1			1			bone & lead
11							1			
12		2	34	1			7	1	3	bone & copper
13			8		1					
14	1	4		10	1					
15							2			

Table 1; Proposed Showcase Contents for Lullingstone Roman Villa Project and Required RH Ranges

Only a proportion of archaeological copper alloy and iron artefacts undergo adverse reactions at ambient RHs with large number of objects showing complete stability. Figure 1 shows the results of a survey of copper alloy artefacts from Ancient Egypt stored in the British Museum. The objects were classified into categories, A to D, where A indicated almost complete stability and D, rapid ongoing deterioration. Collections of objects from the seventeen sites showed very differing stabilities in the ambient storage environment. No site had more than 18% of objects in categories B-D. This high level of stability is likely to be due to the widespread earlier use of chemical stripping treatments in these collections.
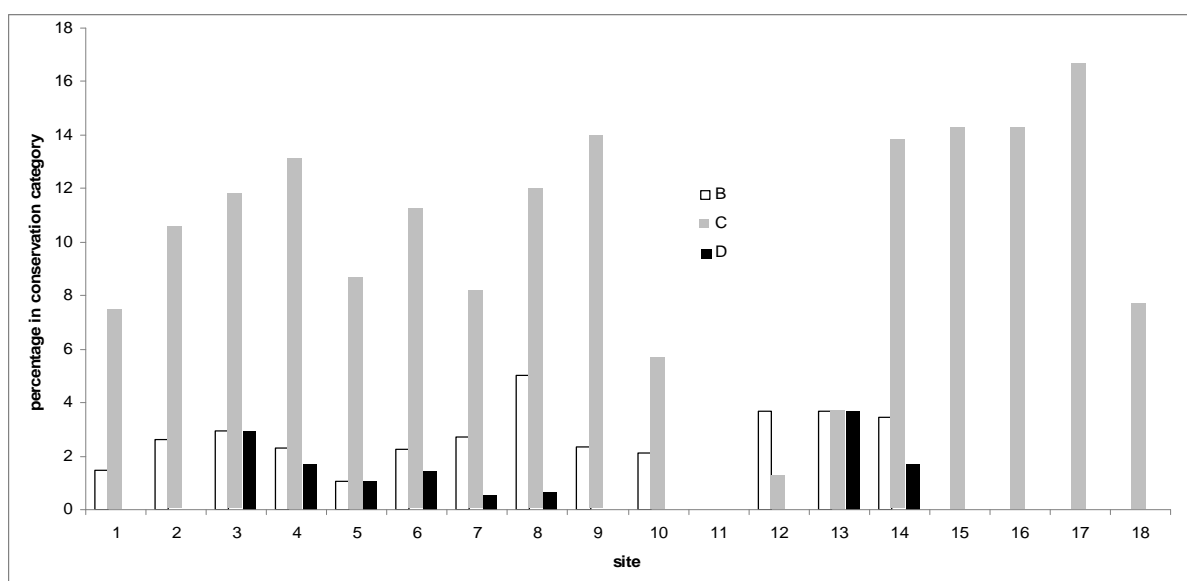

Figure 1; Unstable Copper Alloy Objects from the British Museum's Egyptian Antiquities Collections

Determination of archaeological metal's stability would be of great benefit, allowing precious resources to be targeted towards the objects most in need, reducing display costs and risks to associated materials. Whilst the period of burial, site conditions, metallurgy and shape of the artefacts, burial microenvironments and degree of mineralisation certainly influence the stability, our present understanding is insufficient to predict which artefacts will be stable and which unstable. Methods have been developed or adapted to analyse metal artefacts to predict their stability under ambient conditions.

English Heritage has within its collections a very significant body of architectural stone. Large amounts of this material were collected from its sites during various presentation projects and placed in store without an archaeological assessment, as would be undertaken for freshly excavated material [4]. Much of this material is amorphous in nature and retains no worked surfaces of curatorial interest. A second large corpus of material comprises essentially replicates of simple building features, with little curatorial interest beyond the basic shape information, which has already been recorded. In these instances the stones are being considered for return to their original sites with storage in a turfed, sand clamp above the ground level. This option is only considered for durable sandstones. Sandstone is a highly heterogeneous material and some sandstones would be expected to survive well in the conditions expected within such clamps, whilst others would be expected to undergo slow, but unacceptable, deterioration. X-ray fluorescence and near infra-red spectroscopies have been applied to determine the durability of the sandstones considered. The techniques also form part of the ongoing monitoring process which aims to compare deterioration rates within the clamps and in conventional stores.

ARCHAEOLOGICAL METALS
Radiography
The degree of mineralisation of an iron artefact has been suggested as an indicator of its stability [5]. Radiography is routinely applied to archaeological iron artefacts and multiple radiographs can give an estimate of an artefacts degree of mineralisation. Two recently excavated iron wheel rims for the burial site of Wetwang in Yorkshire were radiographed soon after excavation. Despite showing little evidence of remaining metal cores, they underwent significant deterioration under the ambient room conditions, with akaganeite (β-FeOOH) crystals levering apart the layers of magnetite within six months of excavation. Further investigations were undertaken to understand this. Samples were taken from areas that showed the highest density on the radiographs. Some were prepared as polished cross sections in epoxy resin, carbon coated and examined with scanning electron microscopy with energy dispersive analysis by x-ray, SEM-EDX (Joel 840 with Oxford Instruments Link Isis detector). Parts of the same samples were analysed quantitatively using thermomagnetometry [6]. This technique has a very high sensitivity for elemental iron. Neither technique was able to detect any original iron remaining within the wheel. Although this is a single incidence, it shows that the degree of mineralisation can be a false indicator of stability, at least in some instances. Presumably in this case the iron was at the very end of its corrosion, after 1700 years of burial, and the artefact retained enough iron in solution to start deteriorating when it was exposed to ambient conditions.

The major deterioration reactions of archaeological iron are closely associated with chloride ions. Iron and particularly steels undergo pitting corrosion in high chloride environments. A large proportion of the most deteriorated iron from UK sites show akaganeite spalling from original pits formed during burial and then covered with corrosion products. Investigations into two particularly badly affected site collections showed that information about the pits

were in the original radiographs, taken soon after excavation. No evidence could be made out with the naked eye on the photographic radiographs. However, digitisation and adjustment of the contrast and brightness allowed the pits to be located. The pits had become visible on the artefacts through the akaganeite deterioration process exposing them. The human eye can distinguish between 60 and 80 grey scales, whilst a photograph contains very many more and the 14 bit digitisation system used (Agfa Radview), yields 16,384 greyscales. Newly excavated iron artefacts were also examined in this way. The presence of pits was deduced from radiographs on several objects. The pits were investigated by drilling into the surface of three objects, over 95% of the suspected pits were present. Pale yellow crystals were observed with microscopy at the bases of the pits on the magnetite layer. Analysis with confocal Raman spectroscopy (Renishaw RamanSystem1000 using a 514.5nm Spectra-Physics argon ion laser) identified these to be ferrous chloride. The fluence of the laser was kept below $0.05mJ/cm^2$ to ensure that the iron species did not alter under the photothermal effect. After a few days the edges of the crystals turned brown, analysed as ferric chloride and eventually this expanded to cover the crystals and then converted to akaganeite. Figure 2 shows the Raman spectra of the three species. This provided valuable insight into the deterioration mechanisms of archaeological iron, confirming the theory postulated by Turgoose [7]. The presence of ferric chloride as an intermediate has not been reported. Digital radiography has the potential to detect pits under the iron corrosion layers, indicating a high chloride corrosion environment and very high potential for instability. Differences in corrosion products, artifact geometries and degrees of mineralization do mean that this is a very labour intensive process, requiring much trial and error.
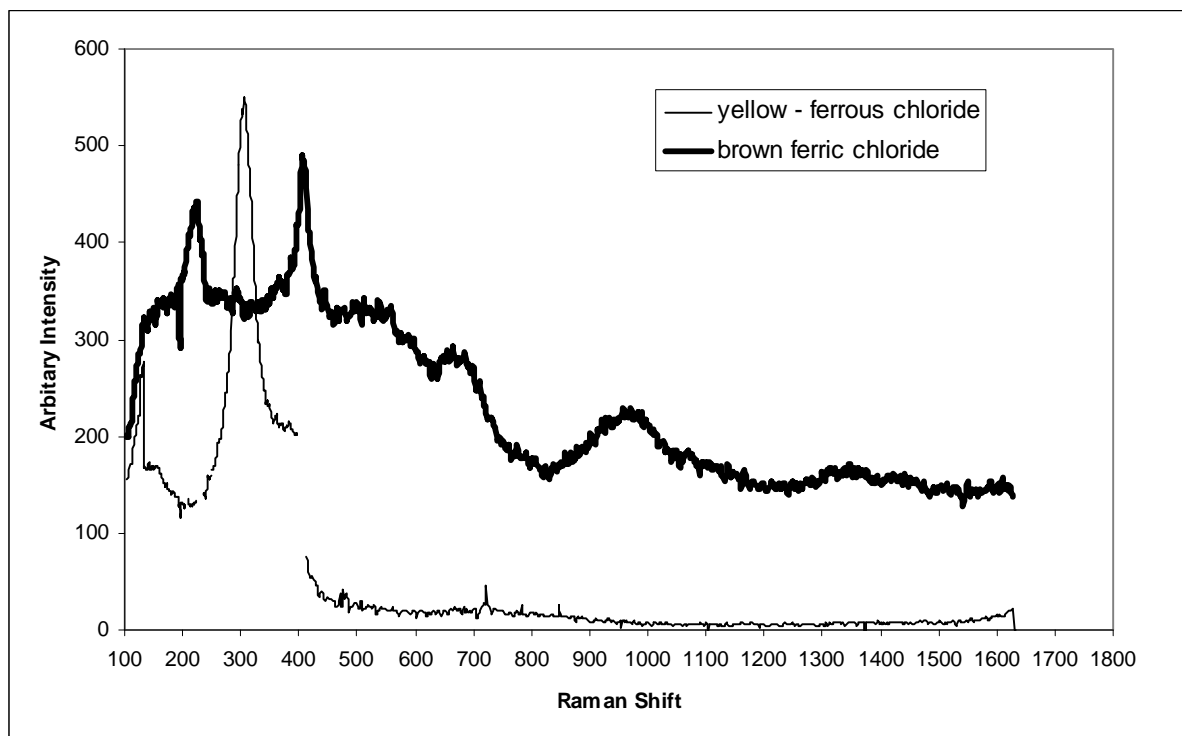

Figure 2; Raman Spectra of Species in the Bottom of Pits

Oxygen Consumption

Oxygen consumption has been used to assess corrosion rates of metals (REFS). This technique was applied to parts of the Wetwang wheel rims. The pieces were placed in a 1000ml glass corrosion jar with Escal film clamped over the top opening. Self adhesive seals were placed over the centre of the Escal to allow sampling of the 5ml of the air within the jar

with a Mapcheck oxygen meter. The RH in the jar was the ambient in the room when the tests were set up, 58-64%. Representative results of six readings taken over three weeks are shown in Figure 3. As can be seen, oxygen is slowly consumed by the deterioration reactions.
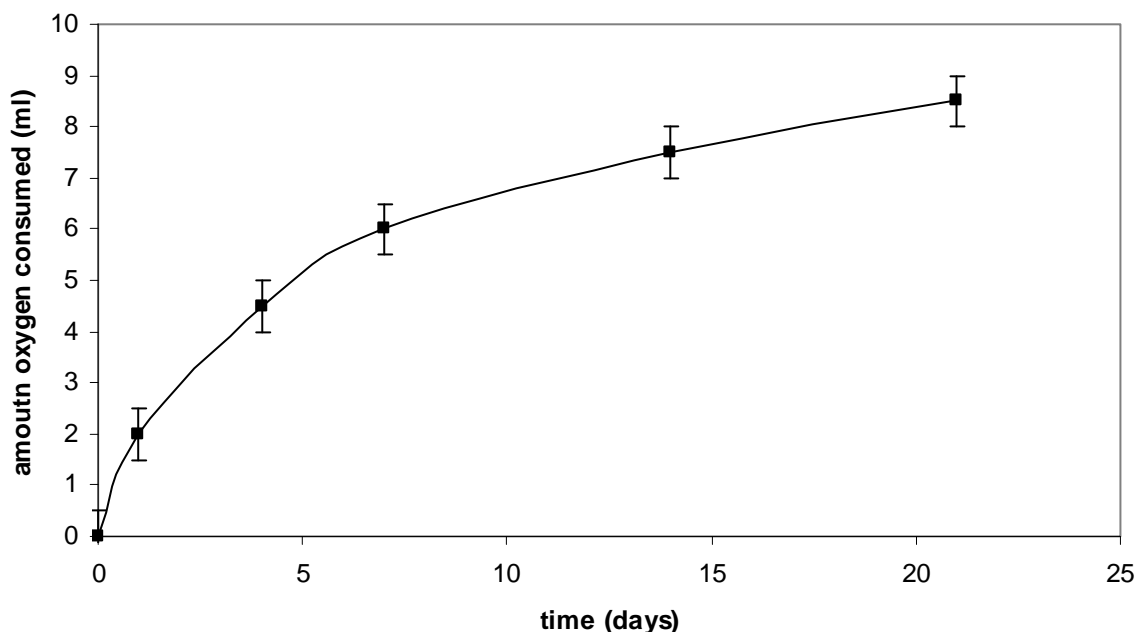

Figure 3; Oxygen Consumed in Deterioration of Wetwang Wheel Fragment

The deterioration processes of archaeological iron are not straight forward metal corrosion reactions and there is still some uncertainty about their exact nature[8,9]. Hence experiments were undertaken to determine the effectiveness of oxygen consumption to measure deterioration rate. It is likely that the deterioration rate of archaeological iron is related to the amount of akaganeite formed. The Raman work reported previously, gives some weight to this assumption. Mixtures of iron and iron (II) chloride powders were exposed to 50% RH in closed conical flasks. The oxygen concentration in the air in the flask was measured with a Gas Sensor Solutions 450 oxygen analyser. This equipment works with Rhuthenium sensors, which fluoresce when illuminated by the analyser. Oxygen quenches the fluorescence. The measurement can be made non-invasively through glass or other transparent materials such as Escal. It removes the requirement to remove an air sample and associated problems with resealing the enclosure and reduced air volume. After various time periods the oxygen concentration was measured, the test opened and a sample of the powder taken. This was analysed quantitatively with FTIR spectroscopy to determine the akaganeite content [10]. Figure 4 shows a good linear relationship between the amount of akaganeite formed and oxygen consumed.
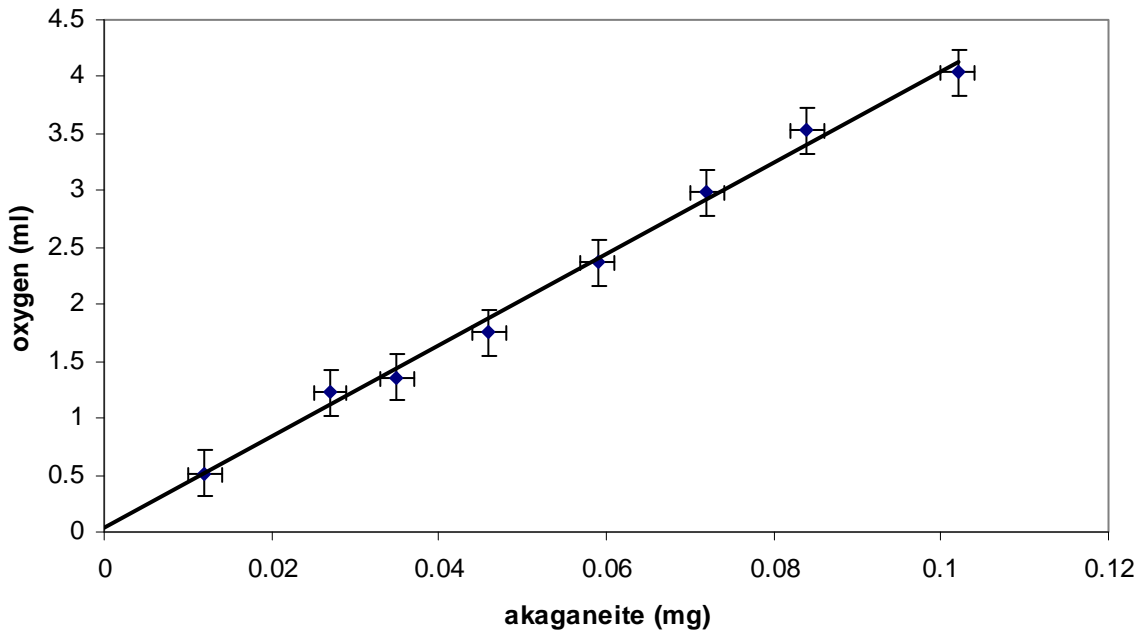
Figure 4; Oxygen Consumed on Akaganeite Formation

In order to test archaeological iron artefacts for ongoing deterioration, a RH of 50% was selected from risk isotherms developed for archaeological iron, see Figure 5. This relatively high value was selected to give detectable oxygen consumption in a short time, whilst limiting the amount of damage caused to the artefacts. The RH is below the threshold at which electrochemical corrosion becomes dominant at ambient temperatures.
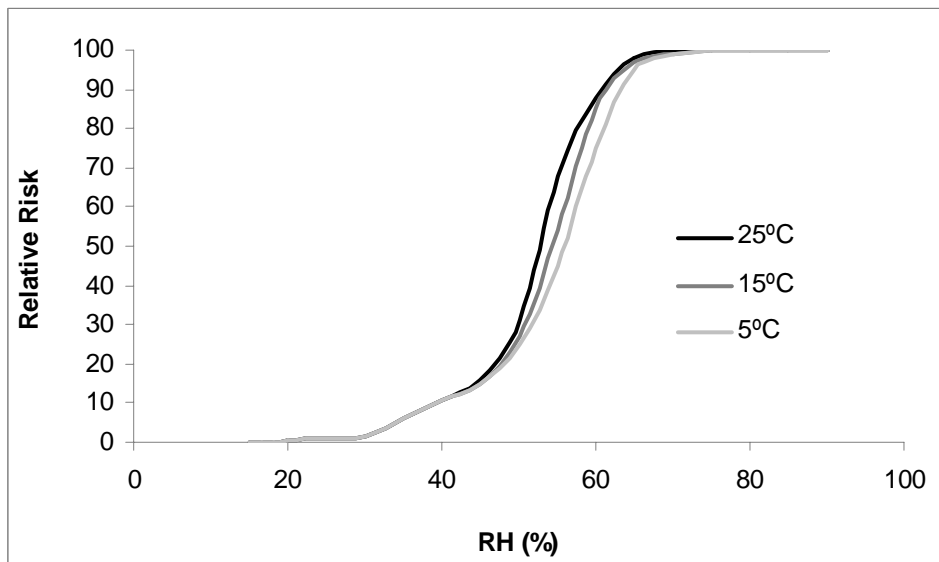

Figure 5; Archaeological Iron Risk Isotherms

The amount of corrosion is also limited by the amount of oxygen in the air in the enclosure and a minimum weight to volume ratio of 0.1g/mil was used in all tests. This RH is also frequently used in controlled showcases within English Heritage and therefore silica gel conditioned to this value is readily available. Tests of smaller artefacts were undertaken in conical flasks with ground glass stoppers providing air tight seals. Vapour permeable Tyvek

was used as a separation layer between artefacts and the Arstorb silica gel used to control RH to prevent the very slight risk of lithium chloride contamination from the Artsorb. Larger objects were encapsulated in heat sealed Escal bags with Artsorb cassettes to control the RH. Approximately 25% of the iron and copper alloy artefacts tested showed no oxygen consumption after two weeks, indicating stability. For the Lullingstone project this meant that cases 6 and 7 could confidently be left at ambient RHs without drying, reducing the risk to the bone artefacts displayed.

SANDSTONE REBURIAL

English Heritage's storage strategy incorporates provision for reburial of certain categories of durable sandstone architectural pieces, as described in the introduction. Analysis has been used both to characterise those types of sandstone that will be durable in the sand clamps being developed, and also to compare the deterioration rates of pieces buried in the clamps and kept in more conventional storage.

Sandstones bound with silaceous material would be expected to have extremely good durability within the clamps. Calcite bound sandstones would be expected to show much lower durability, especially if there was little calcite present or if the calcite crystallite size was small. Sandstones bound with ferruginous material would be expected to show intermediate durability, with the susceptibility to water depending on the exact iron mineral binding. Hematite shows low water solubility, whilst ferrihydrate is more soluble, with limonite having the maximum solubility [11]. The presence of expanding clays in the sandstone would induce swelling and shrinkage cycles in the clamp and reduce durability. Clays also often provide fine scale porosity, making the stone more affected by the action of soluble salts and frost.

X-Ray Fluorescence

X-ray fluorescence (XRF) spectroscopy was applied to sandstones being considered for reburial. The instrument used, Bruker Tracer III was highly portable which facilitated the analysis as many of the large stone pieces were stored on high racking. Often several pieces were stored together on a single pallet and easy manipulation of the hand-held XRF made collecting spectra easy and rapid. The fast collection time, approximately 30 seconds, also facilitated the large number of objects being analysed, over 500 for this study with many more envisaged. XRF has very good sensitivity towards calcium and iron, with excellent detection limits reported. The detection limits were quantified by mixing finely ground calcite (Alfa 98%) and goethite (α-FeOOH, Alfa Aesar 99.98%) powders with quartz (Merck 99.89%) in different proportions. The peak's detection limit was defined as the concentration at which the peak was weaker than three times the background noise. The detection limits determined are shown in Table 2 on the following page.

The XRF equipment was originally designed for analysis of aluminium alloys and can detect this element with the use of a vacuum pump to evacuate the x-ray path. The presence of aluminium strongly indicates the presence of certain species of clay in the sandstone.

Whilst XRF gave a significant amount of information about the sandstones analysed, it does not identify the minerals present. This is particularly important for the iron minerals, with their differing solubility and clays (Cornell 1996). The other major drawback of the technique for this application is its limited information depth. The lower energy x-rays characteristic of light elements, such as aluminium, originate from no more than approximately 10μm from the surface. Whilst more energetic x-rays emitted from iron

originate from deeper depths, the information depth does not exceed 100 μm. Since all of the sandstones analysed had spent some time in the open on sites or buried then surface depleted layers are likely. Calcite is often washed from sandstones to depths exceeding 100 μm, and 3 mm depleted zones have been observed. To overcome the limitations of XRF outlined, near infra red spectroscopy was trialled.

Near Infra-red Spectroscopy
A Perkin Elmer Fourier transform Spectrum One NTS with an Axiom fibre optic probe attachment was used. Spectra were recorded for 32 scans with a resolution of 8cm^{-1}, over a spectral scan range of 12000-4000 cm^{-1}. The region 4000-7600 cm^{-1} was found to contain all eth relevant spectral information. Whilst near infra-red spectroscopy generally produces broad, overlapping absorption bands, often requiring multivariate statistical techniques for quantification, the calcite and clay absorptions were found to be very sharp and well defined, see figure 6.
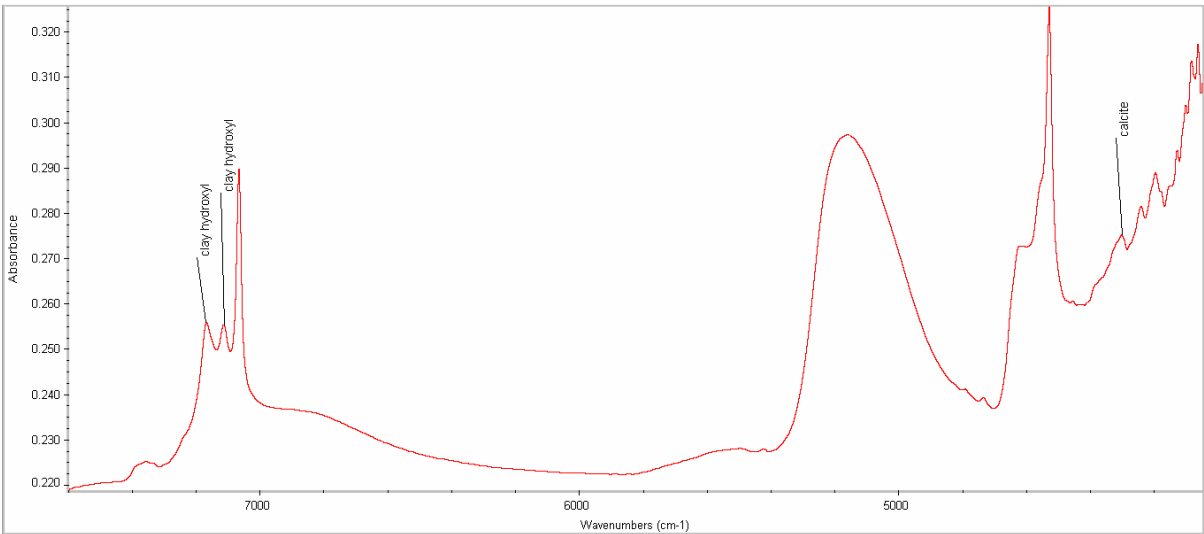

Figure 6;Near Infra-red Spectrum from Sandstone

Hence quantification was undertaken using the Beer Lambert law. This has the advantage of producing a general calibration. Since multivariate techniques use the whole, or large proportions of the spectrum, they are heavily affected by factors such as crystallite size, particle shape and size and alignment and water content. The high variability of sandstones would necessitate a very large multivariate calibration set for this application. The detection limits, defined to ISO11843 [12], were determined, as described previously, and are shown in Table 2.

Hence	NIR			XRF		
Mineral	Peak used	Identification	Detection Limit (%)	Peak used	Identification	Detection Limit(%)
calcite	4280	Overtone	0.0100	3.60keV	Ca Kα	0.0064
goethite	not done			6.41keV	Fe Kα	0.0013
kaolinite	7110	OH stretching	0.0020	1.49keV	Al Kα	0.1600

Table 2; NIR and XRF Quantification and Detection Limits

Infra-red radiation can penetrate materials to a significant depth and the information depth in sandstone would be expected to be hundreds of microns. Initial simple trials with glass slides over a marble piece indicated detection of calcite through several millimetres of glass. These weren't ideal as the marble was 100% calcite, not the less than 1% expected in sandstone. The glass is amorphous, which would minimise scattering of the near infra-red beam, unlike the sandstone quartz grains.. More representative trials were undertaken with pieces of Doddington, Duston, Grinshill, Red Mansfield and Craigleith sandstone. Several analyses were undertaken across a surface of each stone piece to map any variation in calcite distribution. Similar areas were left untreated, or treated with one, two, three or four drops of dilute (1M) hydrochloric acid to deplete calcite in the sandstone. The areas were selected to be far enough apart to avoid horizontal spreading of the acid through the pore structure of the stone. After treatment and drying the stone pieces were cut in half and the distribution of calcite determined by XRF mapping (Eagle II, 40V, 15mA). The information depth for calcite was found to be between 4 and 7mm depending on the stone type.

Artefact Monitoring
Deterioration within the clamps would be expected to be mainly driven by rainwater passing through the sand. The clamps are sited to avoid run off from agricultural land or road salting and in areas sited as far away as possible from industrial pollution plumes, minimising the potential of polluted water. They are located on land with good drainage to minimise the contact time with water. Conventional drilling and salt analysis has been undertaken to assess any salt uptake through burial. Photogrammetry and colorimetry have been undertaken on index pieces to track physical recession of the surfaces and discolouration. Chemical dissolution of the binding matrix is difficult to detect. Whilst sampling, cross sectioning and SEM-EDX analysis is in progress, the interventive nature of this analysis will limit its application. Index objects for reburial and conventional storage have been analysed with NIR and this analysis will be repeated after several years. Non-interventive analyses have further major advantages for this type of work. Their reproducibility is limited only by the accuracy of repositioning and instrumental variability, whilst techniques that require sampling are fundamentally limited by the material's heterogeneity, which for sandstones is often high. Instrument manufacturers have recently made significant improvements in instrumental variability and this can readily be tracked with calibration standards. The quartz and calcite powder mixtures have been retained for this purpose and will be stored under low RH conditions to ensure their stability.

CONCLUSIONS
Both radiography and oxygen consumption have been explored as techniques to determine instability in vulnerable archaeological iron and copper alloys. Whilst radiography shows promise, this application is very time consuming and the measurement of oxygen consumption is more practical. It has been successfully applied to improve preventive conservation for a large mixed archaeology display and will form a valuable tool in further display and storage projects.

XRF and NIR have been successfully applied to rank the durability of a large number of sandstones proposed for reburial and will be of continuing use to quantify their deterioration. XRF is limited for this application through its small information depth, whilst NIR has been shown to give information from at least 3mm into the stone.

The application of non-destructive techniques has tremendous potential to improve preventive conservation for archaeological collections, reducing costs and allowing limited resource to be targeted to where they will provide the most benefit.

REFERENCES

1. Xavier-Rowe A., Fry C. and Stanley B, Power to Prioritise, IIC, 2008, in press
2. Thickett D. and Odlyha M., Assessment of Dry Storage Microenvironments for Archaeological Iron, Williamsburg, 2005, in press
3. Thickett D., Luxford N. and Lambarth S., Development of Show Cases for Archaeological Metals in Aggressive Environments, Metals 07, Rijksmuseum, Amsterdam, 2007 105-109
4. English Heritage, Management of Projects in the Historic Environment, English Heritage, London, 2006
5. Watkinson, D, Degree of Mineralization: Its Significance for the Stability and Treatment of Excavated Ironwork, Studies in Conservation 28(2) 1983, 85-90
6. Thickett D. and Odlyha M., Application of Magnetometry to Corrosion Studies of Archaeological Iron, Journal of Thermal Analysis and Calorimetry, *Vol. 80 (2005),* 567-5719
7. Turgoose, S., Post-Excavation Changes in Iron Antiquities, Studies in Conservation 27 1982, 98-100
8. Watkinson D. and Lewis M.T., Desiccated Storage of Chloride-Contaminated Archaeological Iron Objects, Studies in Conservation 50 2005, 241-252
9. Selwyn, L.S., Sirois, P.J. and Argyropoulos, V., The Corrosion of Excavated Archaeological Iron with Details on Weeping and Akaganeite, Studies in Conservation, 44, 1999, 217-232
10. Thickett D., The use of Infra-red and Raman Spectroscopies for Iron Corrosion Products, Postprints of Sixth Infra-Red Users Group, Florence, 2004, Il Prato Elsevier, Padua: 86-93
11. Cornell, R. M., and Schwertmann, U., The Iron Oxides. Structure, Properties, Reactions, Occurrence and Uses. Weinheim 1996
12. ISO/DIS 11843-1,2 Capability of Detection, ISO/TC69/SC6, ISO Standard, 11843-1, 1995

[Back to Top]