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FISKERTON CONSERVATION MANAGEMENT: ANALYSIS OF MODERN COPPER SAMPLES BURIED FOR 6, 12, 18 AND 30 MONTHS
ARCHAEOLOGICAL CONSERVATION REPORT

Karla Graham and Jim Williams

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SUMMARY

The Fiskerton conservation management project was set up to advise English Heritage and the Environment Agency on the current condition of the archaeological site at Fiskerton and the impact on buried archaeological materials of re-watering the site. A range of modern analogue materials were buried at the site for periods of 6, 12, 18 and 30 months to assess the types and rates of deterioration before and after re-watering. A programme of burial environment monitoring was also undertaken. This report covers the analysis of the 6, 12, 18 and 30 month copper samples and consideration of the burial environment monitoring data available. The appendices form the site archive for the copper samples.

CONTRIBUTORS

Karla Graham and Jim Williams

ACKNOWLEDGEMENTS

Thanks to the tenant farmer Phil Good for providing land access, Tim Langdale-Smith and Lincolnshire County Council for collecting and paying for (LCC) the water monitoring data. Roger Wilkes for providing technical assistance and my colleagues on the project Vanessa Fell and Paul Simpson. Paul Graham for the production of Figure 3.

ARCHIVE LOCATION

English Heritage, Fort Cumberland, Portsmouth.

DATE OF RESEARCH

2003 to 2007

CONTACT DETAILS

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CONTENTS

INTRODUCTION

The Iron Age site of Fiskerton is located in the Witham Valley, Lincolnshire approximately 60km east of Lincoln (NGR TF 050 716). The site was partly excavated in 1981and 2001 and comprises a timber causeway with associated votive metal weapons, tools and other artefacts. The dendrochronology dates for the timber uprights indicate that the causeway was in use in 456BC-321BC (Field and Parker Pearson 2003). Since 2001, geophysical, auger and field walking surveys have been undertaken within the immediate vicinity of the causeway and in the wider River Witham Valley with the aim of characterising the archaeological and palaeoenvironmental aspects of the site (Last forthcoming, Rackham & Williams forthcoming).

Under the Countryside Stewardship Scheme, it was proposed that the agricultural land containing the causeway site would form part of Environment Agency flood management work planned in the area. In 2004, this involved the reversion of the site from arable to grassland creating a natural wildlife habitat and, the blocking of land drains to reduce site drainage and allow the water-tables to rise.

The effects of raising the water levels on the already desiccated soil and on archaeological materials were not known and, it was possible that the introduction of different water chemistry and oxygen regimes would be detrimental to the archaeological site. A conservation management project was therefore set up in 2003 by Vanessa Fell, English Heritage Archaeological Conservator, to advise English Heritage and the Environment Agency on the current condition of the archaeological site and the impact of re-watering (Fell 2003). The two principles project aims are (Fell 2003):

- To determine the impact of re-watering on the preservation of archaeological materials at Fiskerton
- To provide guidance on the future management of archaeological material at Fiskerton.

The specific objectives of the project are (Fell 2003):

- To examine the deterioration in archaeological and experimental samples of a range of materials
- To test methodologies for assessing conditions of a variety of archaeological materials so that these methodologies can be used at other sites in the Witham Valley and elsewhere.
- To formulate a protocol for use in any future excavations carried out at the site.

A burial environment monitoring programme was set up by Jim Williams, English Heritage Regional Science Advisor for the East Midlands to establish baseline conditions before the site was re-watered in 2004. Five groups of boreholes ('clusters') were established along the projected length of the causeway and piezometer tips were inserted at various depths to collect ground water. The composition of the ground water was determined from

August 2003 through a monthly monitoring programme arranged by Jim Williams (Williams 2005). This included measuring pH, redox potential, temperature and chemical composition (sulphate, calcium, chloride, ortho-phosphate, sulphide, silicate, iron, manganese, copper, nitrite, nitrogen) to monitor the effects of changes in water-tables and chemistry of the ground-water which occur as a consequence of these changes (Fell and Williams 2004). To date the water levels and limited water chemistry (redox potential and pH data) have been analysed and reported on in the proceedings of the third international conference Preserving Archaeological Remains in situ (Williams et al 2008). The analysis of the conductivity data and the complete water chemistry data has yet to be undertaken.

Before the site was re-watered, modern experimental materials (iron, copper, bone, red deer antler and cattle horn) were buried in the vicinity of the causeway in December 2003 (Fell et al 2005). They were installed at two locations (Clusters 1 and 2) to specific depths down to a maximum of 1.7 metres (Figure 1). The clusters lie just north and south of the area excavated in 1981: Cluster 1 was located adjacent to the east-west drainage channel (the North Delph) and Cluster 2 was located 50 metres further north. The modern materials were recovered and analysed at regular intervals (6, 12, 18 and 30months) to determine how the process of re-watering affects the survival of different types of materials. The samples analysed at 6 months (June 2004) represent the period before the site was re-watered. The north-south aligned drainage ditches were deliberately blocked in October 2004, 10 months after the samples were buried. The 12 month (December 2004), 18 month (June 2005) and 30 month (June 2006) samples represent the period post re-watering.

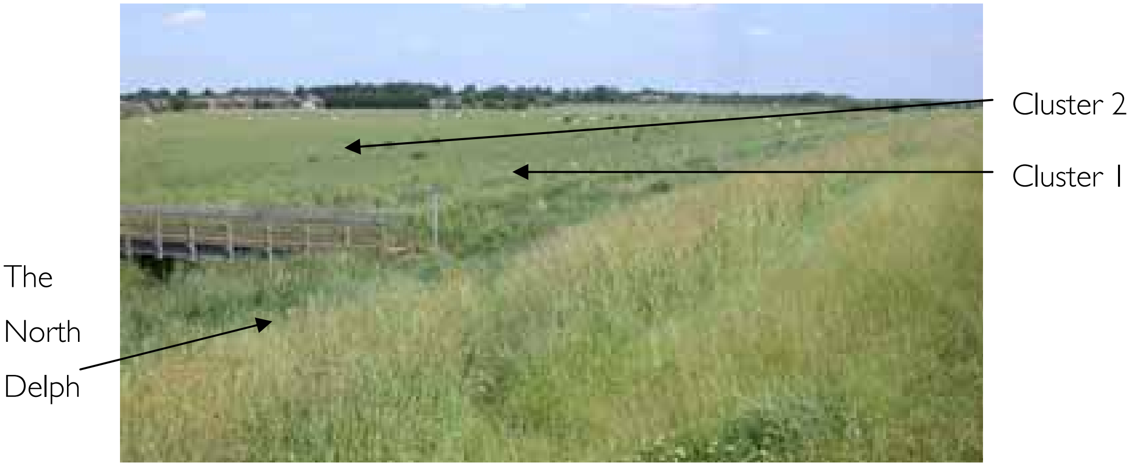


Figure1 The site at Fiskerton showing the location of Cluster 1 and 2 relative to the North Delph

This report covers the analysis of the 6, 12, 18 and 30 month copper samples and a summary of the burial environment monitoring data relevant to the location and duration of burial for the copper samples. A separate report will compare the modern samples with the samples removed from the archaeological copper objects. The background to the project and methodologies for the modern analogue samples and environmental monitoring are covered in an earlier English Heritage report (Fell et al 2005) and therefore only summarised in this report

METHODS

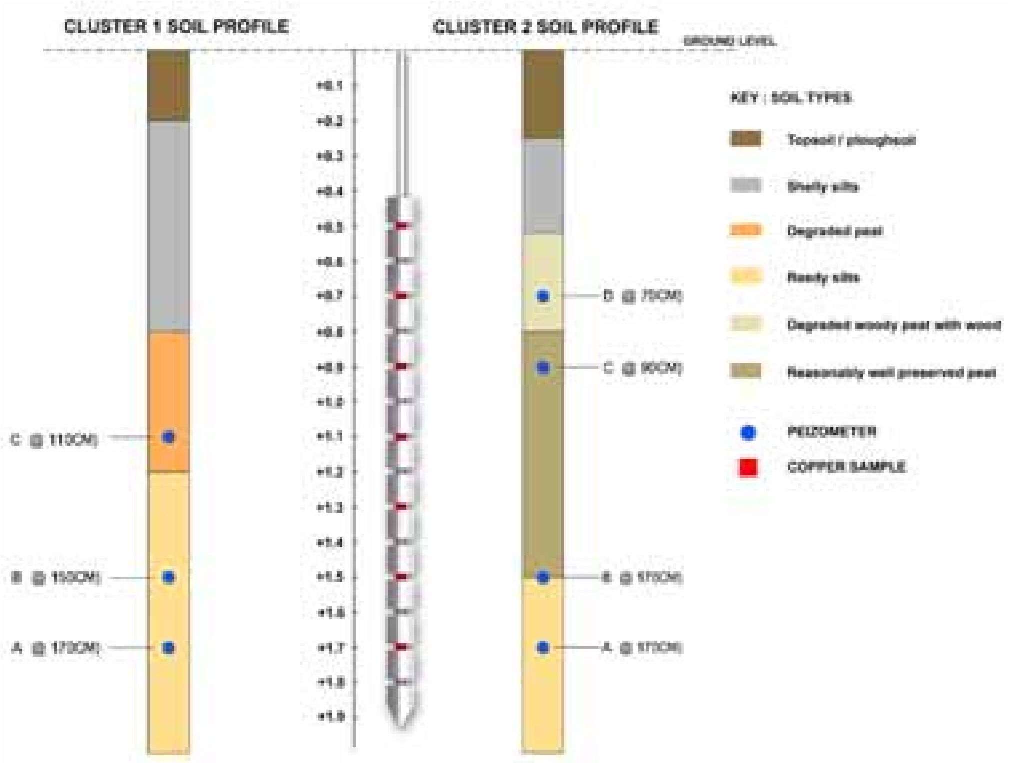
Material description

To directly monitor the reaction of a non ferrous metal with the Fiskerton burial environment, a British Standard unalloyed copper (Unified Numbering System: CW004A / C101) was used (Graham 2005a). 22.2mm diameter copper round bar was cut in 20mm length samples and a 12.4mm hole drilled through.

Sample location

Seven samples were slotted onto solid glass fibre reinforced polyester rods using polypropylene spacers to separate the samples out at 0.5, 0.7, 0.9, 1.1, 1.3, 1.5 and 1.7m depths (refer to Tables 1 and 2, Figures 2 and 3). One rod was removed from each cluster at 6, 12 and18 months and the remaining rods at 30 months (three from cluster 1 and two from cluster 2) based on the original planned end of the burial environment monitoring programme.

Figure 2 Copper rod removed after 30 months burial. The image on the far right shows the copper samples from the top of the soil profile (0.5m depth) through to the bottom of the profile (1.7m depth)



Cluster	Depth (m)	Soil description
1	0 - 0.2	Topsoil / plough soil
	0.2 - 0.8	Shelly silts
	0.8 - 1.20	Degraded peat
	1.20	Top of reedy silts
2	0 - 0.25	Plough soil
	0.25 - 0.52	Shelly silts
	0.52 - 0.80	Degraded woody peat with wood
	0.80 - 1.50	Reasonably well preserved peat
	1.50 - 2.00	reedy silt

Figure 3 Soil profiles at cluster 1 & 2, and locations of piezometers and copper samples (P Graham)

Table 1 Cluster 1 copper sample locations and burial period

Depth (m)	Soil Description	Months Burial	Rod	Sample No.
0.5	Shelly silts	6	1	61
		12	2	62
		18	4	64
		30	3	63
			5	65
			6	66
0.7	Shelly silts	6	1	6
		12	2	12
		18	4	24
		30	3	18
			5	30
			6	36
0.9	Degraded peat	6	1	5
		12	2	11
		18	4	23
		30	3	17
			5	29
			6	35
1.1	Degraded peat	6	1	4
		12	2	10
		18	4	22
		30	3	16
			5	28
			6	34
1.3	Reedy silts	6	1	3
		12	2	9
		18	4	21
		30	3	15
			5	27
			6	33
1.5	Reedy silts	6	1	2
		12	2	8
		18	4	20
		30	3	14
			5	26
			6	32
1.7	Reedy silts	6	1	1
		12	2	7
		18	4	19
		30	3	13
			5	25
			6	31

Table 2 Cluster 2 copper sample locations and burial period

Depth (m)	Soil Description	Months Burial	Rod	Sample No.
0.5	Shelly silts	6	7	67
		12	10	70
		18	8	68
		30	9	69
0.7	Degraded woody peat with wood	6	7	42
		12	10	60
		18	8	48
		30	9	54
0.9	Reasonably well preserved peat	6	7	41
		12	10	59
		18	8	47
		30	9	53
1.1	Reasonably well preserved peat	6	7	40
		12	10	58
		18	8	46
		30	9	52
1.3	Reasonably well preserved peat	6	7	39
		12	10	57
		18	8	45
		30	9	51
1.5	Reedy silt	6	7	38
		12	10	56
		18	8	44
		30	9	50
			11	72
1.7	Reedy silt	6	7	37
		12	10	55
		18	8	43
		30	9	49
			11	71

Recovery and post excavation storage

After removal from the ground, the rods were treated as follows (refer to Table 3)

6 month samples

Each rod was immediately wrapped in polythene sheeting and as much air as possible was excluded before sealing the ends using Duck^{tm} tape. On return to Fort Cumberland, the rods were placed in cold storage until the point of analysis.

12 and 18 month samples

Each rod was dismantled on site and the excess soil removed carefully using Industrial Methylated Spirits (IMS). The samples were photographed using a digital camera before placing in numbered and perforated plastic bags. Samples were placed in pre-prepared bags constructed from Escal^{tm} laminated barrier film. Initially, each sample was placed in a separate Escal^{tm} bag (12 months) and then all the samples from rod placed in one Escal^{tm} bag (18 months). Oxygen scavengers (Revolutionary Preservation (RP) System Type A) and desiccated silica gel were placed in these bags and the units hermetically sealed using an Escal^{tm} clip (Graham 2005b).

30 month samples

As the remaining 3 rods from cluster 1 and 2 rods from cluster 2 had to be removed at the end of the monitoring period, it provided an opportunity to test the performance and value of the different storage methods. All the samples were stored in Escal^{tm} bags. One bag had silica gel and oxygen scavengers in it, one had just silica gel and nothing was placed in the last bag. At cluster 2, a comparison was made between the full system of silica gel and oxygen scavenger and the method of simply placing the samples in unperforated bags sealed in a Stewart^{tm} box in the cold room, Fort Cumberland at approximately 5 degrees Celsius until analysis.

Table 3 Post excavation treatment of copper samples

Cluster	Months burial	Rod	Cold room	Cleaned IMS	Escal™ bag	Silica gel	Oxygen Scavenger
1	6	1	■				
	12	2		🟦	🟩	🟧	◼
	18	4		🟦	🟩	🟧	◼
	30	3		🟦	🟩		
		5		🟦	🟩	🟧	
		6		🟦	🟩	🟧	◼
2	6	7	■				
	12	10		🟦	🟩	🟧	◼
	18	8		🟦	🟩	🟧	◼
	30	9		🟦	🟩	🟧	◼
		11	■				

Analysis

The samples were examined under low powered binocular magnification (x20) and where possible further soil was carefully removed using a scalpel and bamboo stick. The samples were then photographed.

Weight changes

The samples were weighed and the percentage change calculated.

X-Ray Diffraction analysis

X-Ray diffraction analysis was undertaken to identify the corrosion products (crystalline compounds). Under binocular magnification a scalpel was used to remove the corrosion products into a snapfit gelatine capsule (Agar Scientific). The corrosion products were transferred to an agate pestle and mortar, grinded and then sprinkled onto a glass slide. Industrial Methylated Spirits was dropped on the slide to evenly disperse the sample before it evaporated. The XRD analysis was undertaken at Fort Cumberland on a Philips 1830 / 1840 X-ray diffractometer with a Cobalt anode. The XRD program parameters used are summarised in Table 4.

Table 4 X-Ray Diffraction analysis parameters

Parameter (unit)	6 month and archaeological samples	12, 18 and 30 month samples
Time (minutes)	80	50
Generator tension (kV)	40	40
Generator current (mA)	40	40
Wavelength Alpha 1 [Å]	1.78896	1.78896
Wavelength Alpha 2 [Å]	1.79285	1.79285
Start angle [°2Θ]	21.050	15.050
End angle [°2Θ]	69.950	74.950
Step size [°2Θ]	0.1	0.1
Time per step (seconds)	10	5
Type of scan	Continuous	Continuous

Once each scan was complete, the peaks were identified with the aid of the Philips PW1876 PC-Identify software (Version 1.0i, 1999) and X-Pert High Score Square (Version 2.0, 2005). Each scan was run against the International Centre for Diffraction Data (ICDD) database of Powder Diffraction Files (PDF). A Restrictions File was applied to focus the search on copper corrosion products and minerals that were likely to be present. Once complete, the scan was observed against each PDF of minerals that were likely be present to determine if there was a good match between the peaks and the PDF d-spacings. Further PDFs were manually inputted to determine potential matches. Table 5 outlines the range of corrosion products present on the samples with their corresponding Powder Diffraction File numbers.

Table 5 Copper minerals and corrosion products

Mineral name	Description	Formula	Corrosion product colour	Powder Diffraction File (PDF)
Copper	Copper metal	Cu		00-004-836
Cuprite	Copper (I) oxide	Cu_20	Red	00-005-667
Malachite	Copper (II) carbonate hydroxide	$Cu_2(CO_3)(OH)_2$	Green	00-041-1390
Chalcocite	Copper sulphide	Cu_2S	Black	00-033-490
Djurleite	Copper sulphide	$Cu_{31}S_{16}$	Black	00-015-157
Quartz	Silicon dioxide	SiO_2		00-033-1161

RESULTS

Appendices 1 to 4 present the cluster 1 and 2 results by month of burial:

- Appendix 1 6 month results
- Appendix 2 12 month results
- Appendix 3 18 month results
- Appendix 4 30 month results

Each appendix contains the following data:

- Weight changes
- X-Ray Diffraction analysis spectra
- Tabulated XRD results: corrosion products and minerals present classed as major, medium or minor according to the relative intensity for each XRD scan (peak heights).
- A comparison of the corrosion products identified for clusters 1 and 2.

Appendices 5 and 6 present the cluster 1 and 2 results by depth of burial

The main report text contains the following results

- Digital images. All the samples were digitally photographed after removal from the ground and these images are presented in Figures 4 and 5. The images clearly display the difference between the oxidised copper corrosion products (blue-green) and the reduced copper corrosion products (black).
- X-Ray diffraction analysis results. Figure 6 summarises all the X-Ray Diffraction analysis results for both cluster 1 and 2 allowing for a direct comparison between the two clusters.
- Burial environment monitoring results
- Storage method results

Digital images

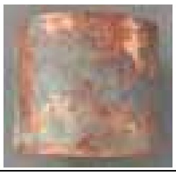
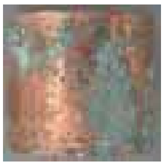
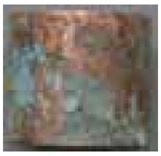
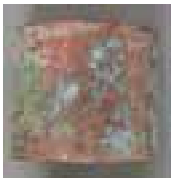
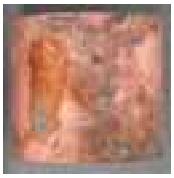
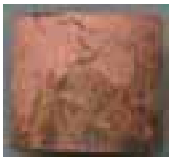
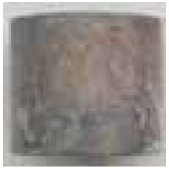
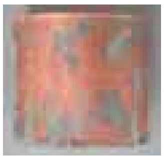
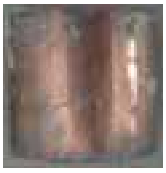
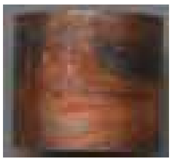
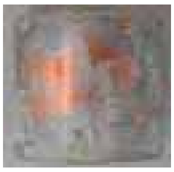
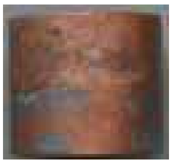
Depth (m)	6 months	12 months	18 months	30 months
0.5	Lost			
0.7	Lost			
0.9				
1.1				
1.3				
1.5				
1.7				

Figure 4 Digital images of cluster 1 samples after removal from the ground.

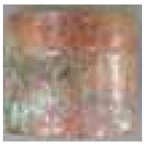
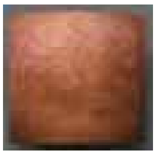
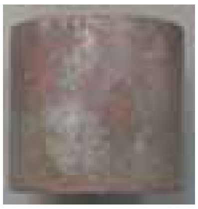
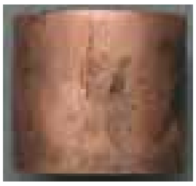
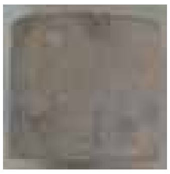
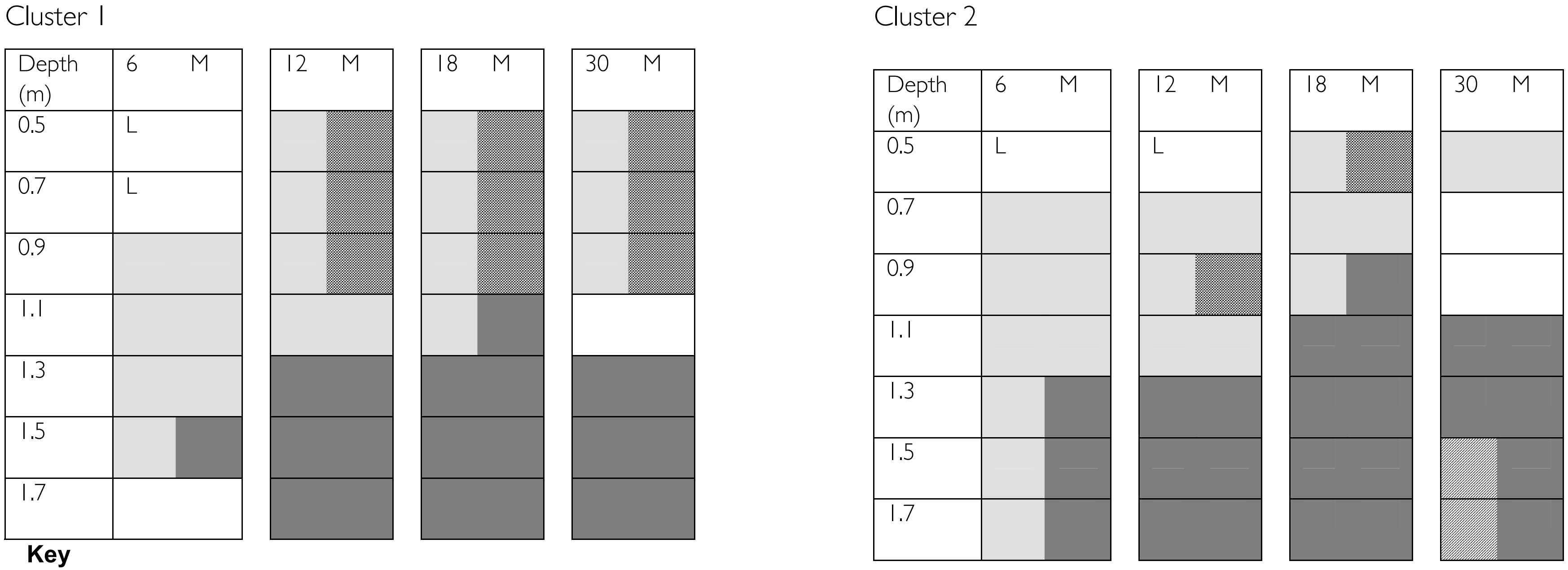
Depth (m)	6 months	12 months	18 months	30 months
0.5	Lost	Lost		
0.7				
0.9				
1.1				
1.3				
1.5				
1.7				

Figure 5 Digital images of cluster 2 samples after removal from the ground.

X-Ray diffraction analysis results



Key

M	Months
□	No corrosion products
░	Copper oxide: Cuprite Cu_2O
▩	Copper carbonate: Malachite $Cu_2CO_3(OH)_2$
■	Copper sulphide: Chalcocite Cu_2S
▨	Copper sulphide: Djurleite $Cu_{31}S_{16}$
L	Sample lost during recovery

Figure 6 Copper results for clusters 1 and 2: major copper corrosion products identified through XRD analysis. Each column represents a sample, removed from the ground at 6, 12, 18 and 30 months, clusters 1 & 2. Corrosion products are identified in the key. In some cases, 2 corrosion products occur at the same depth (i.e. cluster 1, 6 months, depth 1.5m)

Burial environment monitoring results

The burial environment monitoring results presented here are limited to water levels and water chemistry (pH and redox potential) at Clusters 1 and 2 covering the period from just before the copper samples were buried (October 2003) to the point when the 30 month copper samples were removed (June 2006). The pH and redox potential measurements, relying upon the availability of water, are limited to the lower horizons (1.5 and 1.7m). The water level and chemistry results are discussed in more depth elsewhere (Williams et al 2008).

Water levels

Water levels were measured from piezometers at each cluster (refer to Figure 3): three at cluster 1 (Depths 1.7, 1.5 and 1.1m) and four at cluster 2 (Depths 1.7, 1.5, 0.9 and 0.7m). Figures 7 and 8 present the water levels measured below ground for clusters 1 and 2 along with the water level of the nearby North Delph. For the whole monitoring period (October 2003 to June 2006), the water level ranged between 0.67m to 1.6m below ground level at cluster 1 and between -0.21m and -1.62m below ground level at cluster 2.

Before the land drains were blocked, the average water level was 1.15m below ground at cluster 1 (range 0.96m to 1.46m below ground) and 1.01m below ground at cluster 2 (range 0.67m to 1.62m below ground). After the land drains were blocked in October 2004 the water level rose at both clusters: the average water level rose to 0.72m below ground at cluster 1 (range 0.67m to 1.6m below ground) and to 0.44m below ground at cluster 2 (range 0.21m to 0.65m below ground). The difference in water levels between the two clusters can be accounted for by the proximity of the cluster 1 to the North Delph and its drawdown effect on the water levels.

Figure 9 is an updated version of figure 6 showing the X-Ray Diffraction analysis results for each cluster with the addition of the water levels data for each cluster i.e. the presence or absence of water down the burial horizon (dry, wet or a zone of fluctuating water level).

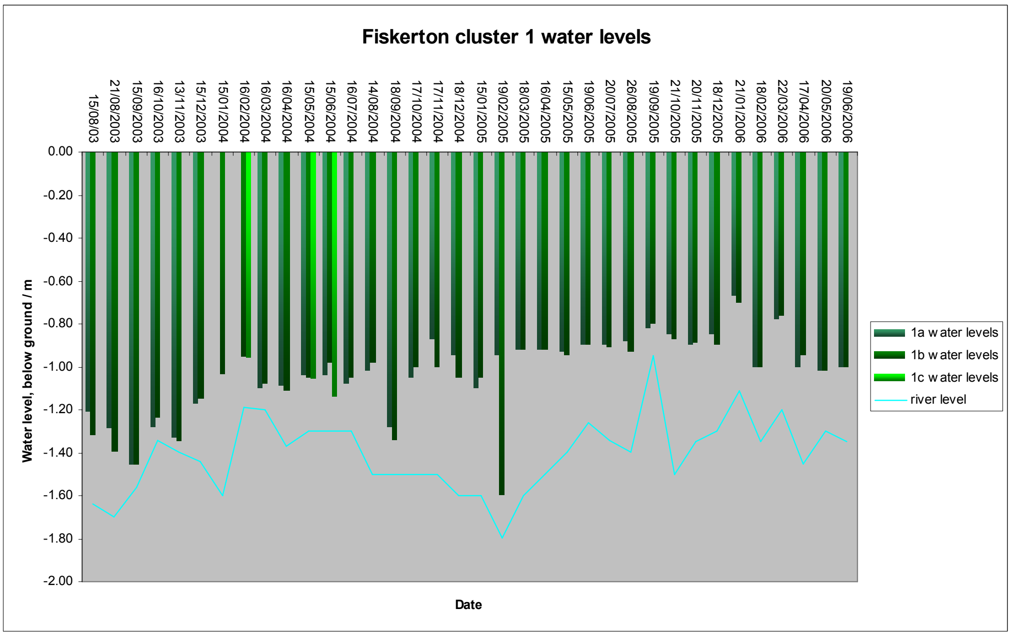


Figure 7 Cluster 1 water levels below ground (measured from three piezometers) and river level. Piezometer 1a at 1.7m depth, 1b at 1.5m depth and 1c at 1.1m depth.

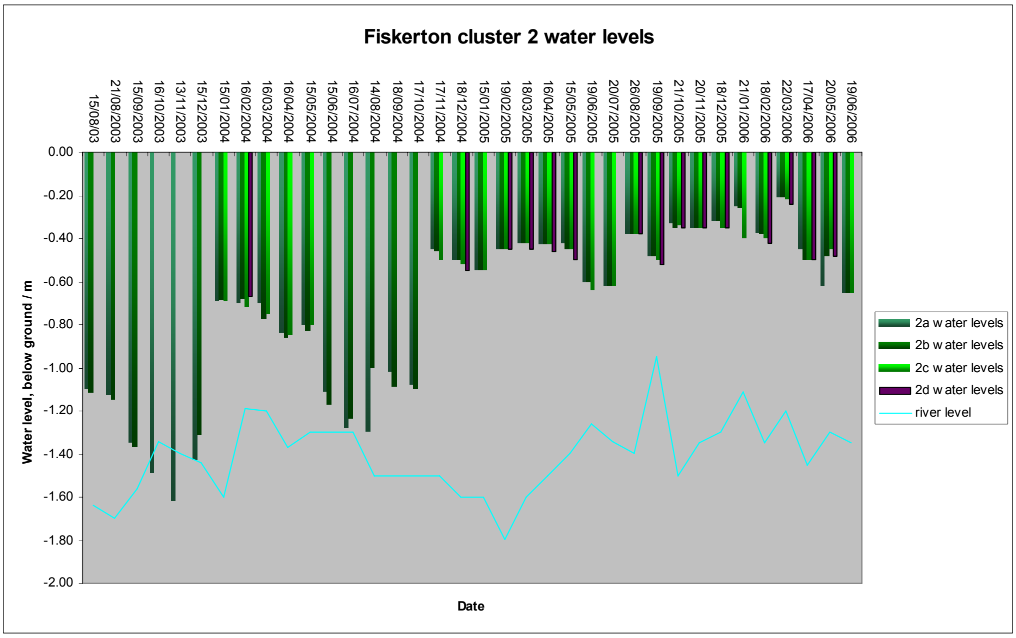
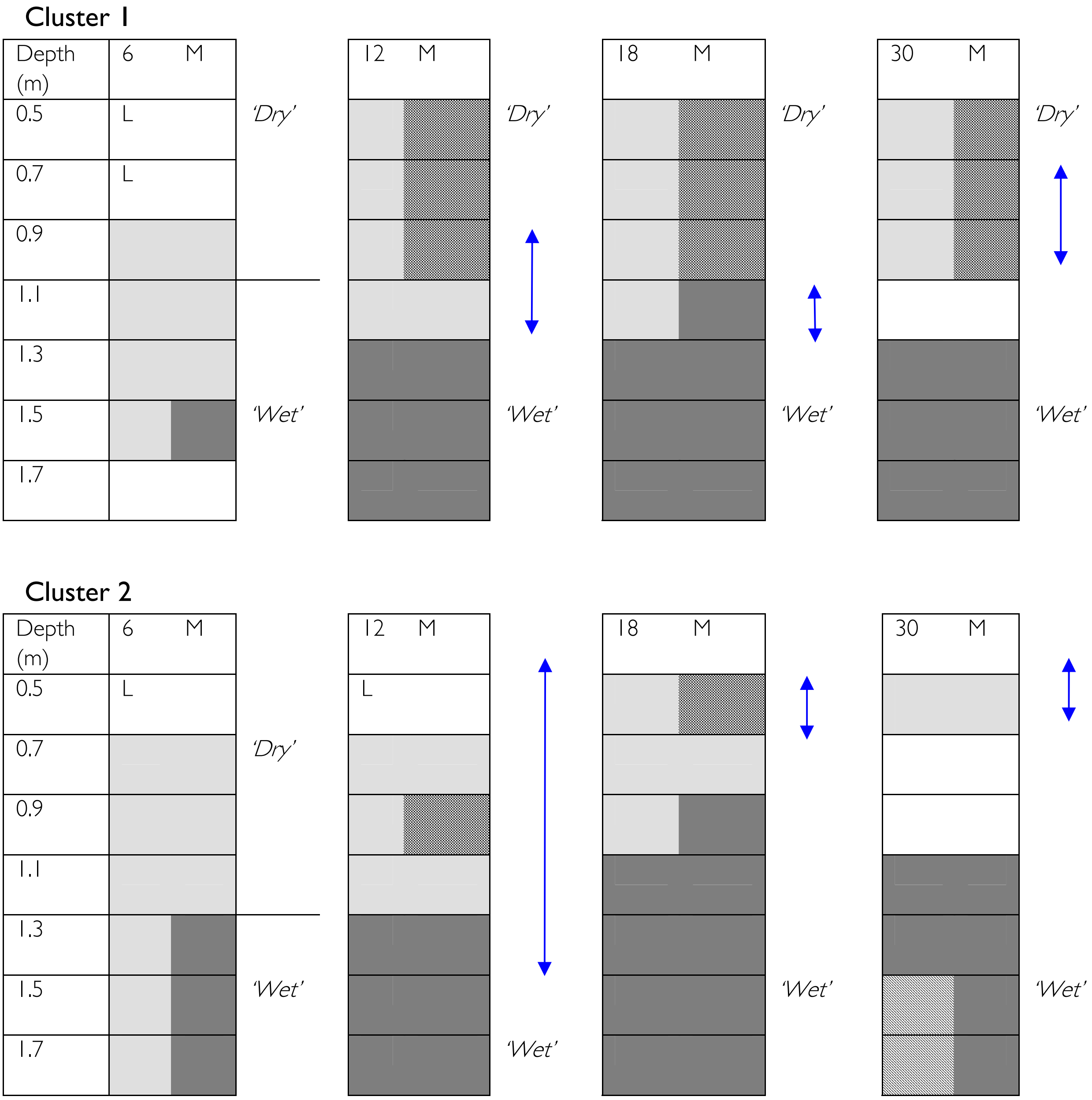


Figure 8 Cluster 2 water levels below ground (measured from four piezometers) and river level. Piezometer 2a at 1.7m depth, 2b at 1.5m depth, 2c at 0.9m depth and 2d at 0.7m depth.



Key

M	Months	▨	Copper sulphide: Djurleite $Cu_{31}S_{16}$
□	No corrosion products	L	Sample lost during recovery
░	Copper oxide: Cuprite Cu_2O	Dry	Water not present
▩	Copper carbonate: Malachite $Cu_2CO_3(OH)_2$	Wet	Water present
■	Copper sulphide: Chalcocite Cu_2S	↔	Fluctuating water levels
▨	Copper sulphide: Djurleite $Cu_{31}S_{16}$		

Figure 9 Copper results for clusters 1 and 2: major copper corrosion products identified through XRD analysis. Each column represents a sample, removed from the ground at 6, 12, 18 and 30 months, clusters 1 & 2. The presence, absence or movement of water level in the horizon (during the burial period) is indicated to the right of each sample column.

pH and redox potential

Water samples were removed from the piezometers at both clusters for pH and redox potential measurements (1.5 and 1.7m depth at cluster 1 and at 0.7, 0.9, 1.5 and 1.7m depth at cluster 2). The results are presented in Figures 10 and 11. For the purpose of directly comparing the clusters, only the 1.5 and 1.7m depth results for each cluster are considered below.

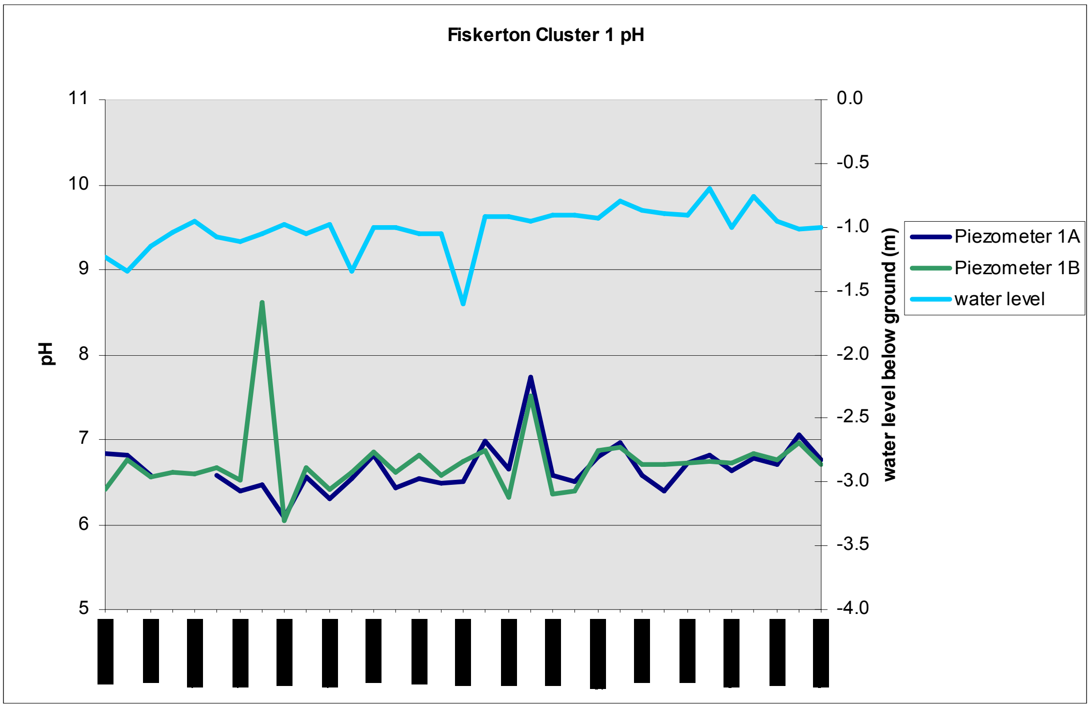
pH

Before the land drains were blocked, the average pH at cluster 1 was 6.54 pH at 1.7m depth (range 6.09 to 6.83pH) and 7.28 pH at 1.5m depth (range 6.05 to 8.61 pH). At cluster 2 the average pH was 6.66pH at 1.7m depth (range 5.98 to 7.78 pH) and 6.31pH at 1.5m depth (range 5.86 to 6.88pH).

After the land drains were blocked, the average pH at both the cluster 1 depths was more or less the same: it become slightly less acidic at 1.7m depth: 6.72pH (range 6.4 to 7.74pH) and it increased in acidity at 1.5m depth: 6.74pH (range 6.33 to 7.52pH). At cluster 2 the average pH at 1.7m depth became slightly more acidic at 6.53pH (range 6.23 to 6.9pH). At 1.5m depth there was almost no change: 6.33pH (range 5.85 to 6.97pH).

Redox potential

At both clusters (1.5 and 1.7m depth), the redox potential ranged between -100mV and +100mV (with some deviation outside of this) and the conditions can be described as moderately reducing (Patrick & Mahapatra 1968).



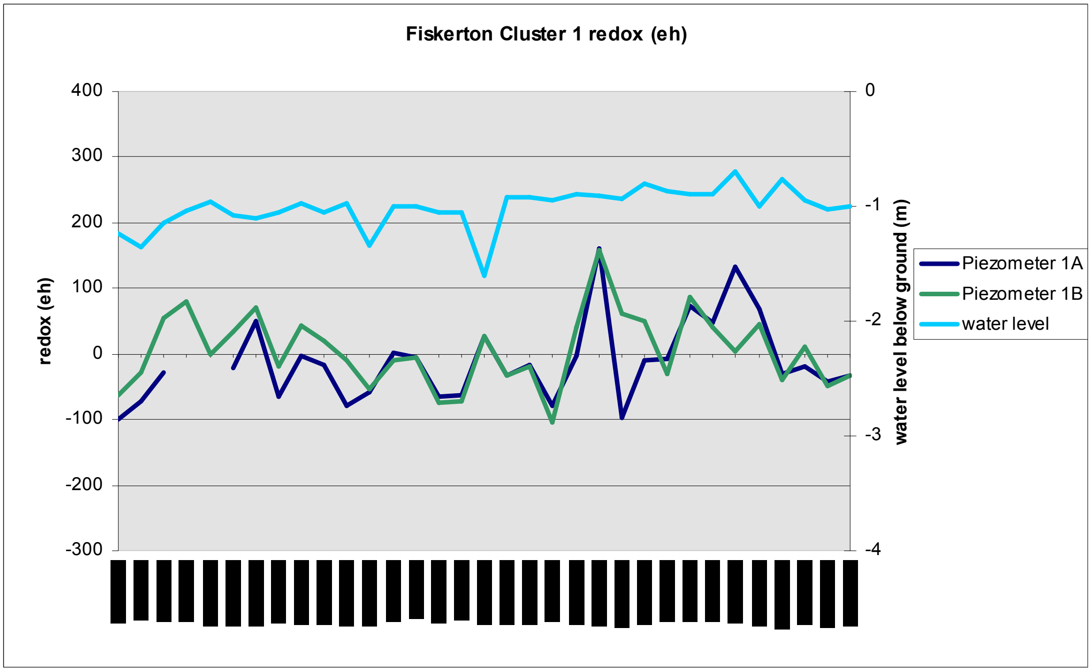
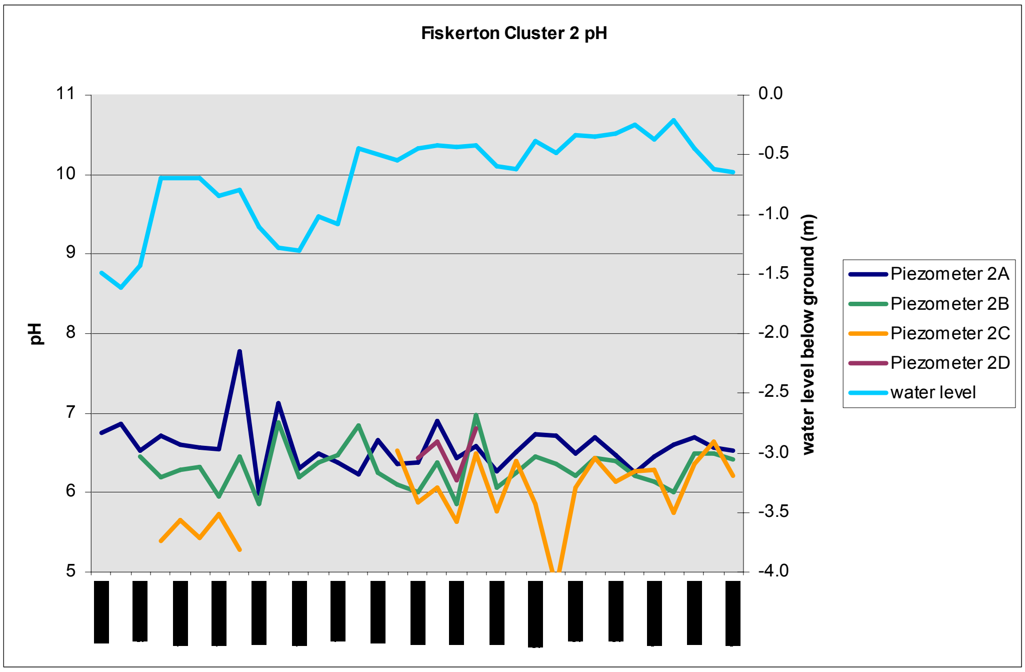


Figure 10 Cluster 1 pH and redox potential measurements against water level below ground (Cluster 1A: 1.7m depth, 1B: 1.5m depth



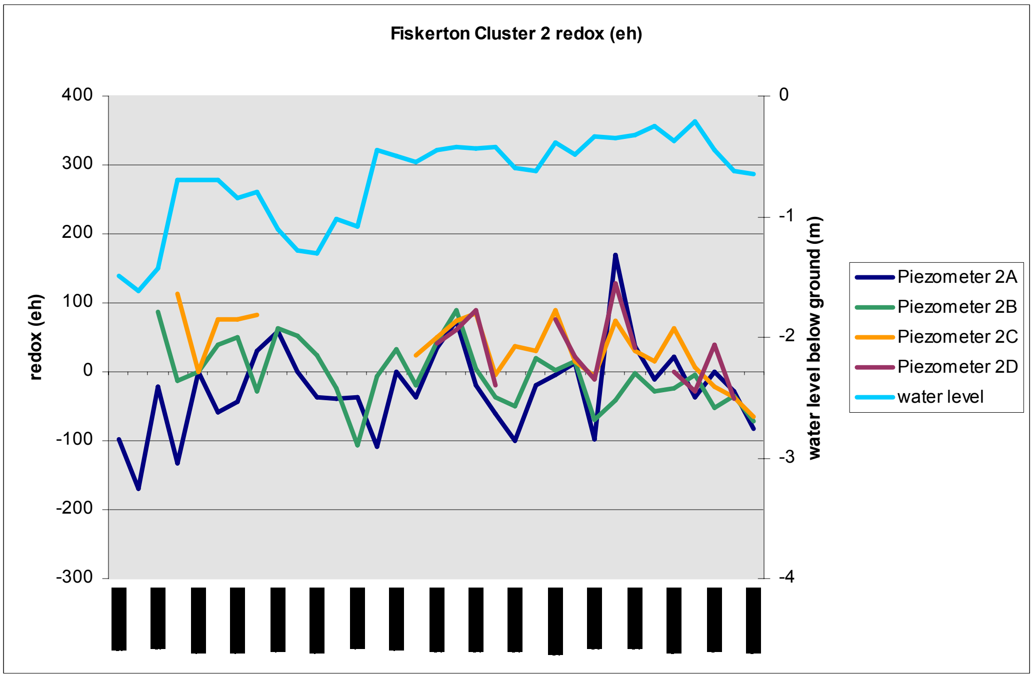


Figure 11 Cluster 2 pH and redox potential measurements against water level below ground (Cluster 2A: 1.7m depth, 2B: 1.5m depth, 2C: 0.9m depth, 2D: 0.7m depth)

Storage method results

At the 30 month sample collection, it was necessary due to site management reasons to remove all the remaining copper sample rods (three at cluster 1 and two at cluster 2). This presented the opportunity to test different post-recovery storage methods to determine if they influenced the type of corrosion products observed on the samples.

The cluster 1 30 month samples were all stored in an Escal^{tm} barrier film bag containing either silica gel, silica gel and oxygen scavengers or, nothing. The results (table 6) show that, apart from the 1.1m samples, the major corrosion products detected through X-Ray Diffraction analysis were the same for the three types of storage methods. Chalcocite was detected on the 1.1m depth samples stored with either nothing or silica gel but no corrosion products were detected on the sample stored with silica gel and oxygen scavengers. The 1.1m depth samples were within the zone of fluctuating water levels and this could simply reflect the loss of corrosion products from this particular sample due to the physical and chemical instability of this part of the horizon rather than as a result of the storage method.

The cluster 2 samples from 1.5 and 1.7m depths were stored in either a Stewart^{tm} box in the cold room or, in an Escal^{tm} barrier film bag containing silica gel and oxygen scavenger. There was also no difference in the corrosion products observed for these samples. The number of variables between the storage methods for these two samples is however too great to comment on the influence of the storage methods. This was a limited study which was undertaken when an opportunity presented itself and a more comprehensive study (comparing all the parameters over a longer period of time) would be required to arrive at full conclusions.

Table 6 30 month samples: comparing different methods of post-recovery storage. Major copper corrosion products identified through X-Ray Diffraction analysis.

Cluster 1

Depth (m)	Rod	Storage method	Sample No.	Cuprite *Copper oxide*	Malachite *Copper carbonate hydroxide*	Chalcocite *Copper sulphide*	Djurleite *Copper sulphide*	Quartz
0.5	3	Nothing	63	░	▓			
	5	SG	65	░	▓			
	6	SG/O_2	66	░	▓			
0.7	3	Nothing	18	░	▓			▨
	5	SG	30	░	▓			▨
	6	SG/O_2	36	░	▓			▨
0.9	3	Nothing	17	░	▓			
	5	SG	29	░	▓			
	6	SG & O_2	35	░	▓			
1.1	3	Nothing	16			▒		
	5	SG	28			▒		▨
	6	SG & O_2	34					
1.3	3	Nothing	15			▒		▨
	5	SG	27			▒		
	6	SG & O_2	33			▒		
1.5	3	Nothing	14			▒		▨
	5	SG	26			▒		▨
	6	SG & O_2	32			▒		▨
1.7	3	Nothing	13			▒		▨
	5	SG	25			▒		▨
	6	SG & O_2	31			▒		▨

Cluster 2

1.5	9	SG & O_2	50			■ or	■	
	11	Cold	72	░			■	
1.7	9	SG & O_2	49			■ or	■	
	11	Cold	71	░			■	

Key to storage methods:

Nothing	Escal^{tm} bag	SG & O2	Escal^{tm} bag, silica gel, oxygen scavenger
SG	Escal^{tm} bag, silica gel	Cold	Stewart^{tm} box, cold room

DISCUSSION

Typical behaviour of copper in the burial environment

In oxidising burial environments the copper (I) oxide cuprite (Cu_20) will initially form next to the surface of the copper (Scott 1997). As the corrosion proceeds this layer builds up becoming less coherent and, in the presence of carbonates further reaction of the metal takes place. Copper II compounds, such as the basic copper carbonate hydroxide, malachite ($Cu_2CO_3(OH)_2$) may form.

In reducing (low oxygen) burial environments little or no corrosion happens. Where sulphate reducing bacteria are present, copper sulphides such as chalcocite (Cu_2S) can occur (Duncan & Ganiaris 1987; McNeil & Little 1999). Alternatively, in reducing acidic environments with chloride ions present, copper chlorides such as nantokite (CuCl) may form. This latter corrosion product is pitting in nature and in the post excavation environment can lead to an aggressive form of corrosion known as 'bronze disease' (Scott 1990).

Cluster 1

At 6 months copper oxides were present on the samples down to 1.5m, copper sulphides were also present on the 1.5m sample and, no corrosion products occurred on the 1.7m sample (refer to Figure 6). For the 12 to 30 month samples, the composition of the corrosion products remained consistent in both the three uppermost samples (copper oxide and copper carbonate hydroxide) and the three lowest samples (copper sulphides). This suggests that oxidising conditions in the upper level and reducing conditions in the lower level were maintained through this period. The corrosion products on the 1.1metre samples indicate that the conditions changed from oxidising at 12 months (copper oxides) to reducing at 18 months (copper sulphides). No corrosion products were detected on the 1.1m sample at 30 months. Fluctuating water levels at 1.1m may have caused both physical instability (the wetting and drying cycles causing the corrosion products to detach from the sample) and chemical instability (the rate of water exchange or change between wet and dry conditions causing the reaction or dissolution of corrosion products as the sample and, or corrosion products try to reach equilibrium with their environment).

Cluster 2

At 6 months copper oxides were present on all the samples down to 1.7m and copper sulphides were already present on the three lowest samples (refer to Figure 6). The presence of both copper oxides and copper sulphides at a depth of 1.3 to 1.7m indicates that the oxides were probably a product of the burial methodology with oxygen being introduced at the time of burial. Between 12 to 30 months, the copper oxides receded up the horizon (from 1.1m depth at 12 months to 0.5m at 30 months) and the copper sulphides occurred higher up the horizon (from 1.3m depth at 6 months to 0.9m at 18 months). At 30 months no corrosion products were present on the 0.7 and 0.9m depth samples. The changes in corrosion products correlate with the recorded rise in water level at cluster 2 from 10 months and related to this, conditions that are conducive to the formation of reduced copper species i.e. moderately reducing conditions.

CONCLUSION

Archaeological copper alloys will have formed layers of corrosion products that will affect their stability within the burial environment and may prevent or reduce the rate at which dissolution of the metal occurs. To establish a baseline from which to monitor reactions, the copper samples went into the Fiskerton burial environment clean and free of any surface patinas. The corrosion products are therefore not truly representative of the processes that buried archaeological material would be subject to. The 6 month samples will for example represent the immediate period of adjustment of clean copper to new environmental conditions and the formation of surface patinas. Ideally, there should have been several sample collections before the re watering occurred in order to establish a proper baseline.

Overall, at Fiskerton the level of copper corrosion was low. At cluster 1 the composition of the corrosion products remained relatively unchanged over the six to thirty month burial period with copper oxides and copper carbonate hydroxides present above the water table and copper sulphides present below it. The change in corrosion products on the 1.1 metre cluster 1 samples from oxidising at 12 months (copper oxides and copper carbonate hydroxides) to reducing at 18 months (copper sulphides) correlates with the time when rewatering occurred, and whilst the North Delph continued to exert considerable influence on the water levels, the average level rose from 1.15m before rewatering to 0.72m afterwards, with a reduction in seasonal fluctuation (Williams et al 2008).

In the cluster 2 samples a similar change from oxides to sulphides was recorded in the 0.7m to 1.1m depth samples, again suggesting a change from oxidising to reducing conditions. Little or no corrosion happens in reducing burial environments but in the presence of sulphate reducing bacteria, sulphides can occur (Duncan and Ganiaris 1987; McNeil and Little 1999). This was the situation below the water table at both clusters, where the absence of corrosion products at the level of the fluctuating water level suggests that although water levels have risen as a result of the rewatering, seasonal fluctuations in water supply are still causing physical and chemical instability. The composition of the soil profile at each cluster (and associated physical and chemical properties) may have also influenced the distribution of corrosion products. At cluster 1 for example, degraded peat is recorded between 0.85 and 1.2m whereas at cluster 2 reasonably well preserved peat is recorded at 0.8 to 1.5m.

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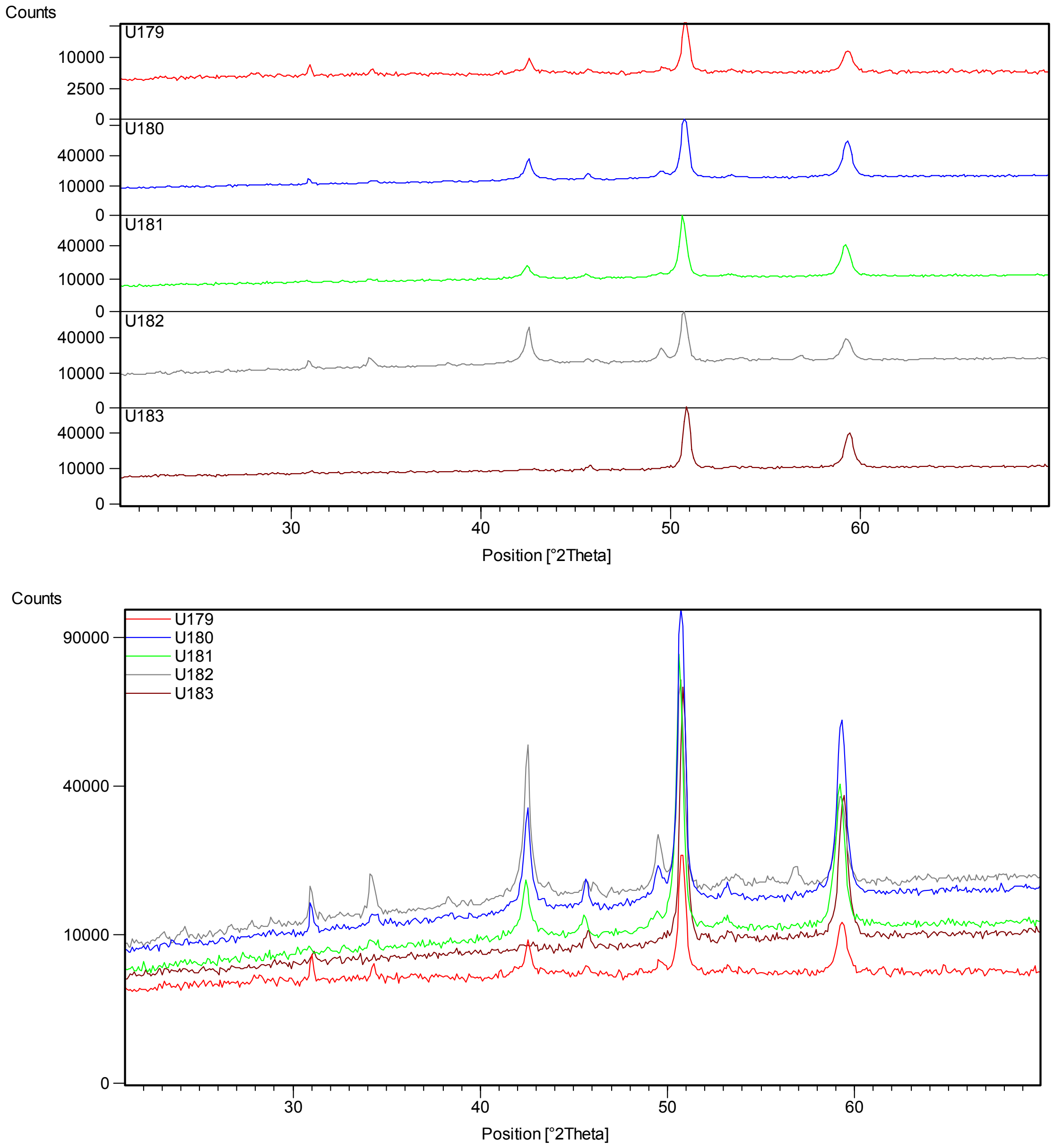
APPENDIX 1: 6 MONTH SAMPLES

Table 7 Weight changes for the Cluster 1, 6 month samples (Rod 1)

Depth (m)	Sample No.	Weight(g) Before	Weight (g) After	Difference
0.5	61	47.60	Lost	
0.7	6	47.89	Lost	
0.9	5	47.02	47.04	0.02
1.1	4	47.31	47.32	0.01
1.3	3	47.50	47.51	0.01
1.5	2	46.34	46.34	0
1.7	1	47.14	47.14	0

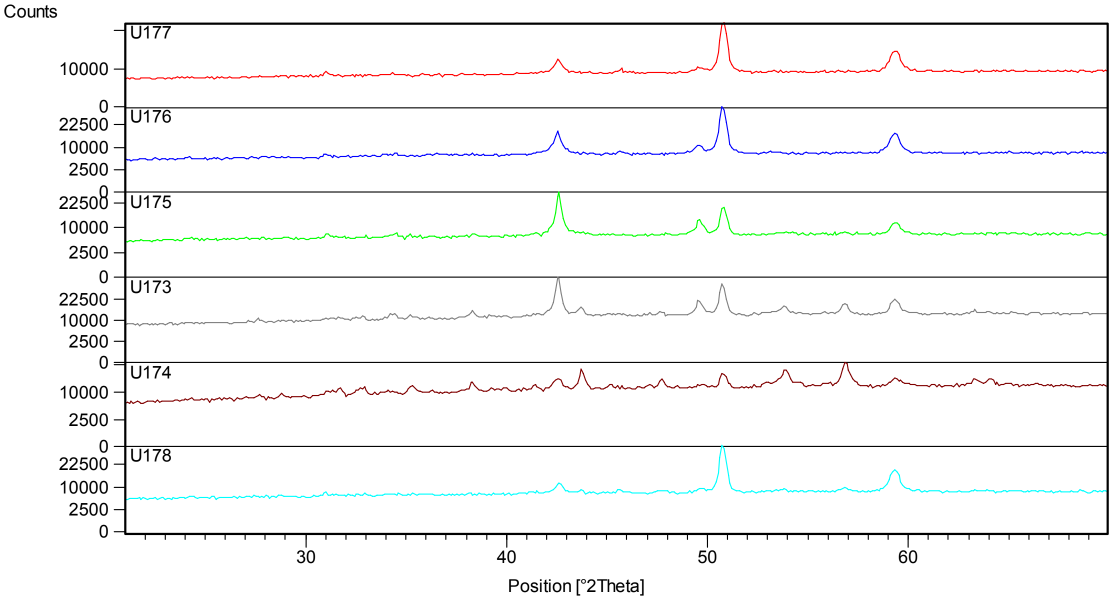
Table 8 Weight changes for the Cluster 2, 6 month samples (Rod 7)

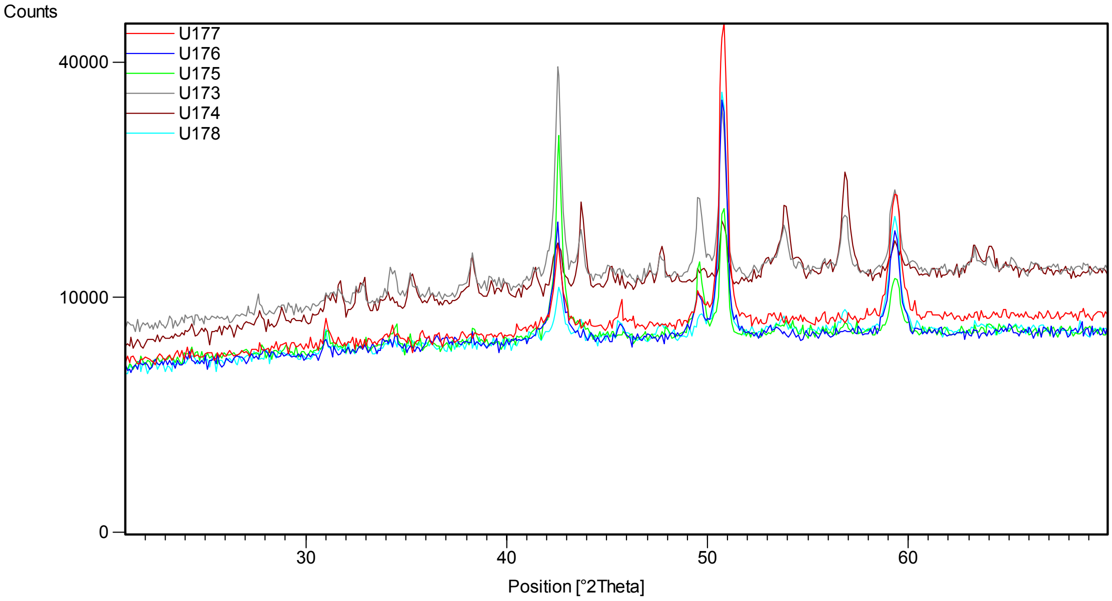
Depth (m)	Sample No.	Weight(g) Before	Weight (g) After	Difference
0.5	67	48.19	Lost	
0.7	42	47.59	47.60	0.01
0.9	41	46.62	46.62	0
1.1	40	47.12	47.12	0
1.3	39	46.87	46.90	0.03
1.5	56	46.13	46.14	0.01
1.7	37	46.90	46.91	0.01



Cluster	Months burial	Rod	Depth (m)	XRD Scan
1	6	1	0.5	
			0.7	
			0.9	U179
			1.1	U180
			1.3	U181
			1.5	U182
			1.7	U183

Figure 12 Cluster 1 XRD spectra for copper samples: 6 months, depths 0.5 to 1.7m





Cluster	Months burial	Rod	Depth (m)	XRD scan
2	6	7	0.5	
			0.7	U177
			0.9	U176
			1.1	U175
			1.3	U173
			1.5	U174
			1.7	U178

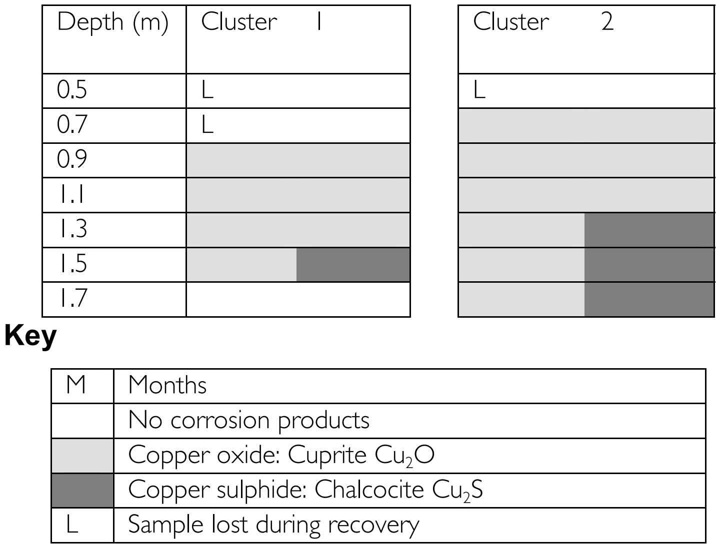
Figure 13 Cluster 2 XRD spectra for copper samples: 6 months, depth 0.5 to 1.7m

Table 9 Cluster 1, 6 month XRD analysis results

Depth (m)	Sample No.	XRD Scan	Major	Medium	Minor
0.5	61				
0.7	6				
0.9	5	U179	Copper	Cuprite	Quartz
1.1	4	U180	Copper	Cuprite	Quartz
1.3	3	U181	Copper	Cuprite	
1.5	2	U182	Copper	Cuprite	Chalcocite, Quartz
1.7	1	U183	Copper		

Table 10 Cluster 2, 6 month XRD analysis results

Depth (m)	Sample No.	XRD scan	Major	Medium	Minor
0.5	67				
0.7	42	U177	Copper	Cuprite	Quartz
0.9	41	U176	Copper	Cuprite	Quartz
1.1	40	U175	Cuprite	Copper	
1.3	39	U173	Cuprite	Copper, Chalcocite	
1.5	38	U174	Chalcocite	Copper, Cuprite	
1.7	37	U178	Copper	Cuprite, Chalcocite	Quartz



Depth (m)	Cluster 1	Cluster 2
0.5	L	L
0.7	L	░
0.9	░	░
1.1	░	░
1.3	░	░ ▓
1.5	░ ▓	░ ▓
1.7		░ ▓

Key

M	Months
	No corrosion products
░	Copper oxide: Cuprite Cu_2O
▓	Copper sulphide: Chalcocite Cu_2S
L	Sample lost during recovery

Figure 14 Copper results for 6 months: major copper corrosion products identified through XRD analysis. The columns each represent a rod removed from cluster 1 or 2. The corrosion products are identified in the key, in some cases, two products occur at the same depth (i.e. cluster 1, depth 1.5m)

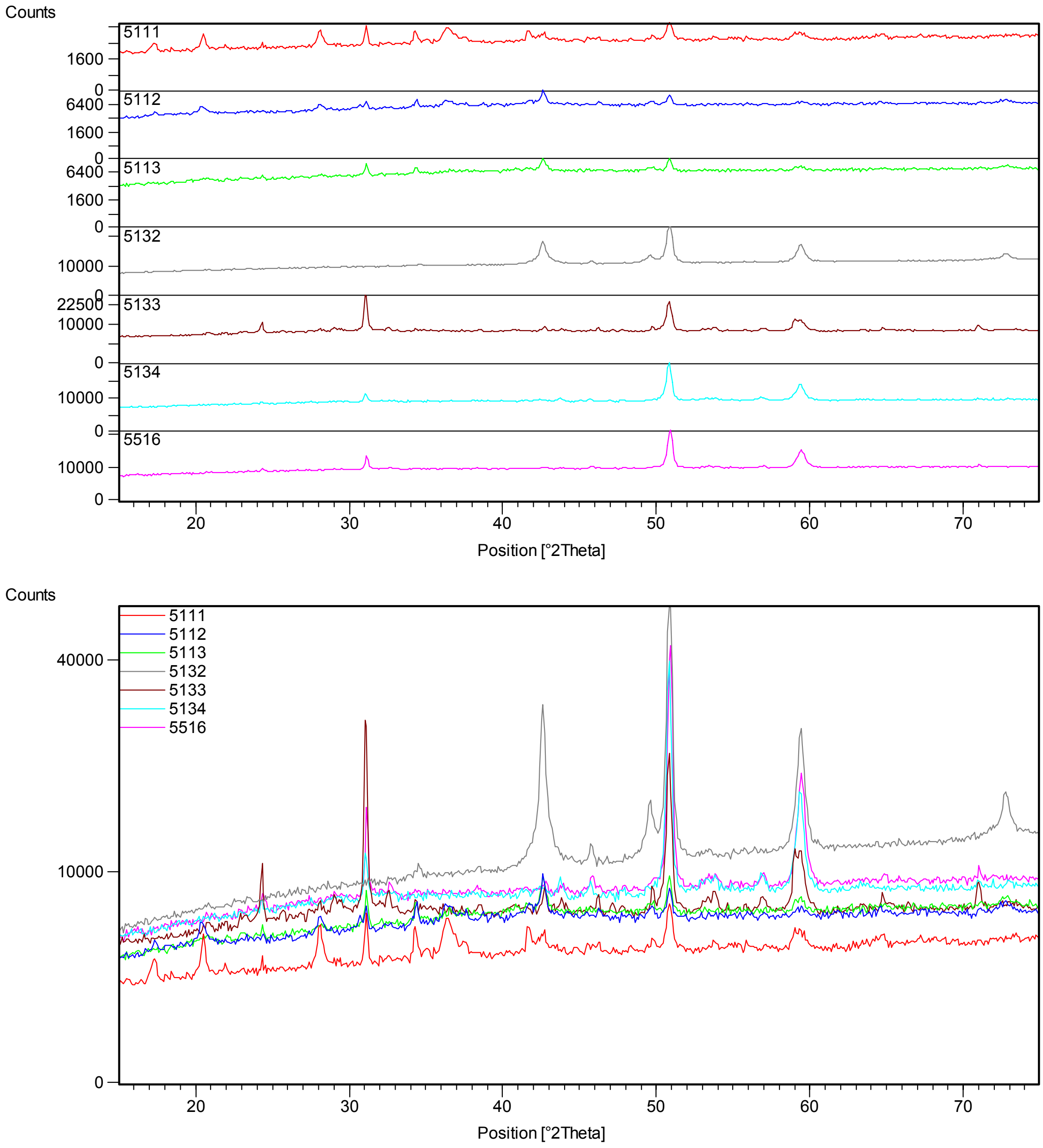
APPENDIX 2: 12 MONTHS

Table 11 Weight changes for the Cluster 1, 12 month samples (Rod 2)

Depth (m)	Sample No.	Weight(g) Before	Weight (g) After	Difference
0.5	62	46.68	not taken	
0.7	12	47.31	47.32	0.01
0.9	11	47.41	47.42	0.01
1.1	10	46.85	46.87	0.02
1.3	9	47.61	47.64	0.03
1.5	8	46.60	46.64	0.04
1.7	7	46.78	not taken	

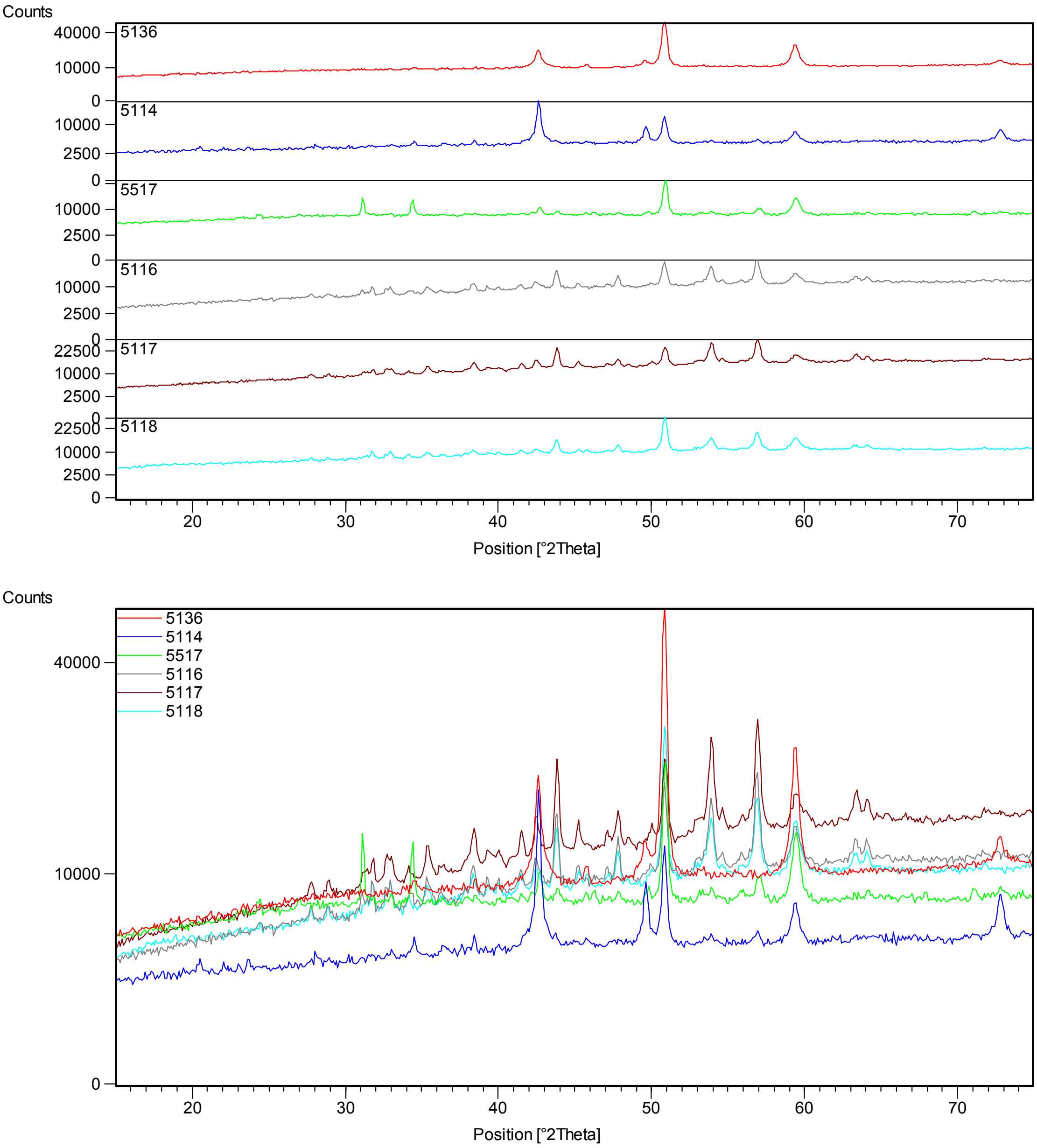
Table 12 Weight changes for the Cluster 2, 12 month samples (Rod 10)

Depth (m)	Sample No.	Weight(g) Before	Weight (g) After	Difference
0.5	70	47.48	Lost	
0.7	60	46.87	not taken	
0.9	59	47.31	47.34	0.03
1.1	58	47.56	not taken	
1.3	57	47.07	47.10	0.03
1.5	44	46.84	46.75	-0.09
1.7	55	46.72	46.73	0.01



Cluster	Months burial	Rod	Depth (m)	XRD Scan
1	12	2	0.5	5111
			0.7	5112
			0.9	5113
			1.1	5132
			1.3	5133
			1.5	5134
			1.7	5516

Figure 15 Cluster 1 XRD spectra for copper samples: 12 months, depth 0.5 to 1.7m



Cluster	Months burial	Rod	Depth (m)	XRD scan
2	12	10	0.5	
			0.7	5136
			0.9	5114
			1.1	5517
			1.3	5116
			1.5	5117
			1.7	5118

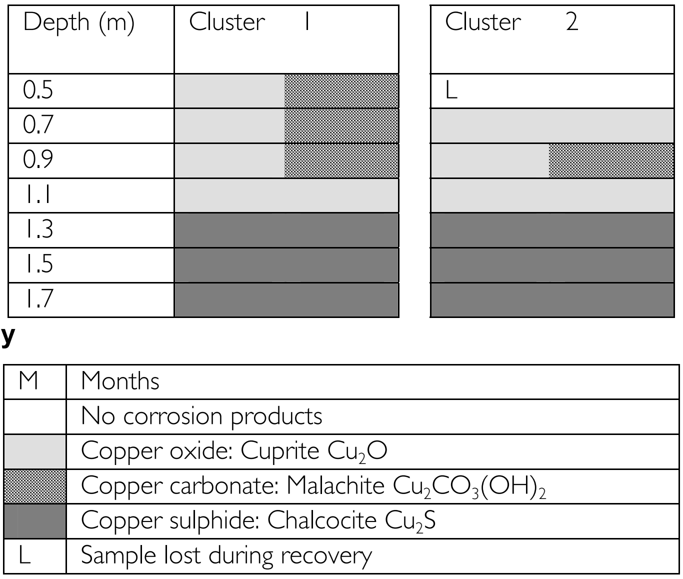
Figure 16 Cluster 2 XRD spectra for copper samples: 12 months, depth 0.5 to 1.7m

Table 13 Cluster 1, 6 month XRD analysis results

Depth (m)	Sample No.	XRD Scan	Major	Medium	Minor
0.5	62	5111	Malachite	Cuprite, Copper, Quartz	
0.7	12	5112	Cuprite	Quartz, Copper, Malachite	
0.9	11	5113	Copper, Cuprite	Quartz	Malachite.
1.1	10	5132	Copper	Cuprite	
1.3	9	5133	Quartz	Copper	Chalcocite
1.5	8	5134	Copper	Quartz	Chalcocite
1.7	7	5516	Copper	Quartz	Chalcocite

Table 14 Cluster 2, 6 month XRD analysis results

Depth (m)	Sample No.	XRD scan	Major	Medium	Minor
0.5	70				
0.7	60	5136	Copper	Cuprite	
0.9	59	5114	Cuprite	Copper	Malachite
1.1	58	5517	Copper	Cuprite, Quartz	
1.3	57	5116	Chalcocite	Copper	
1.5	56	5117	Chalcocite	Copper	
1.7	55	5118	Copper	Chalcocite	



Depth (m)	Cluster 1	Cluster 2
0.5	░ ▒	L
0.7	░ ▒	░
0.9	░ ▒	░ ▒
1.1	░	░
1.3	▓	▓
1.5	▓	▓
1.7	▓	▓

Key

M	Months
	No corrosion products
░	Copper oxide: Cuprite Cu_2O
▒	Copper carbonate: Malachite $Cu_2CO_3(OH)_2$
▓	Copper sulphide: Chalcocite Cu_2S
L	Sample lost during recovery

Figure 17 Copper results for 12 months: major copper corrosion products identified through XRD analysis. The columns each represent a rod removed from cluster 1 or 2. The corrosion products are identified in the key, in some cases, two products occur at the same depth (i.e. cluster 1, depth 0.5m)

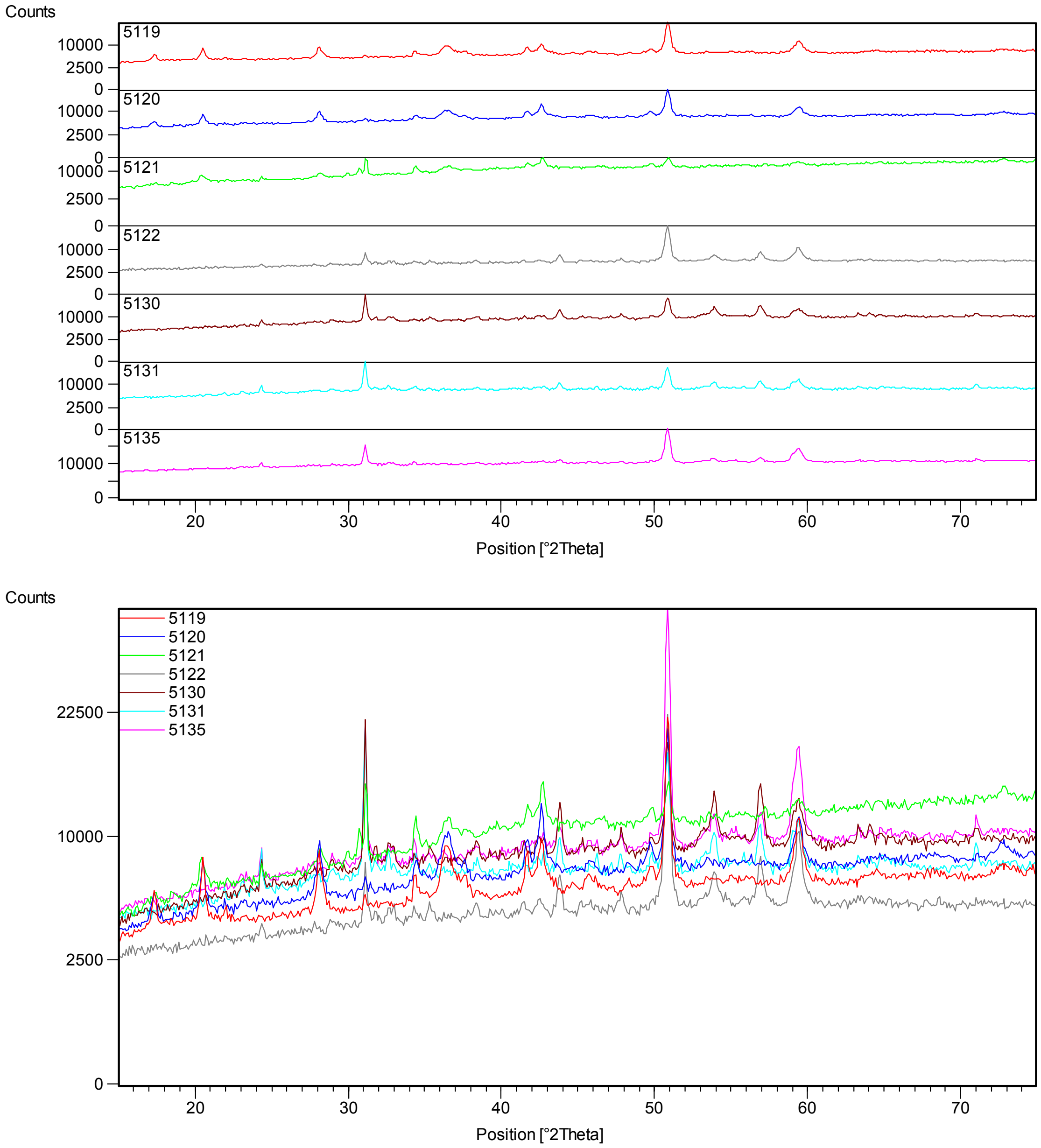
APPENDIX 3: 18 MONTHS

Table 15 Weight changes for the Cluster 1, 18 month samples (Rod 4)

Depth (m)	Sample No.	Weight(g) Before	Weight (g) After	Difference
0.5	64	46.75	46.77	0.02
0.7	24	46.15	46.15	0
0.9	23	47.89	47.90	0.01
1.1	22	47.08	47.09	0.01
1.3	21	47.91	47.92	0.01
1.5	20	47.97	48.02	0.05
1.7	19	47.65	not taken	

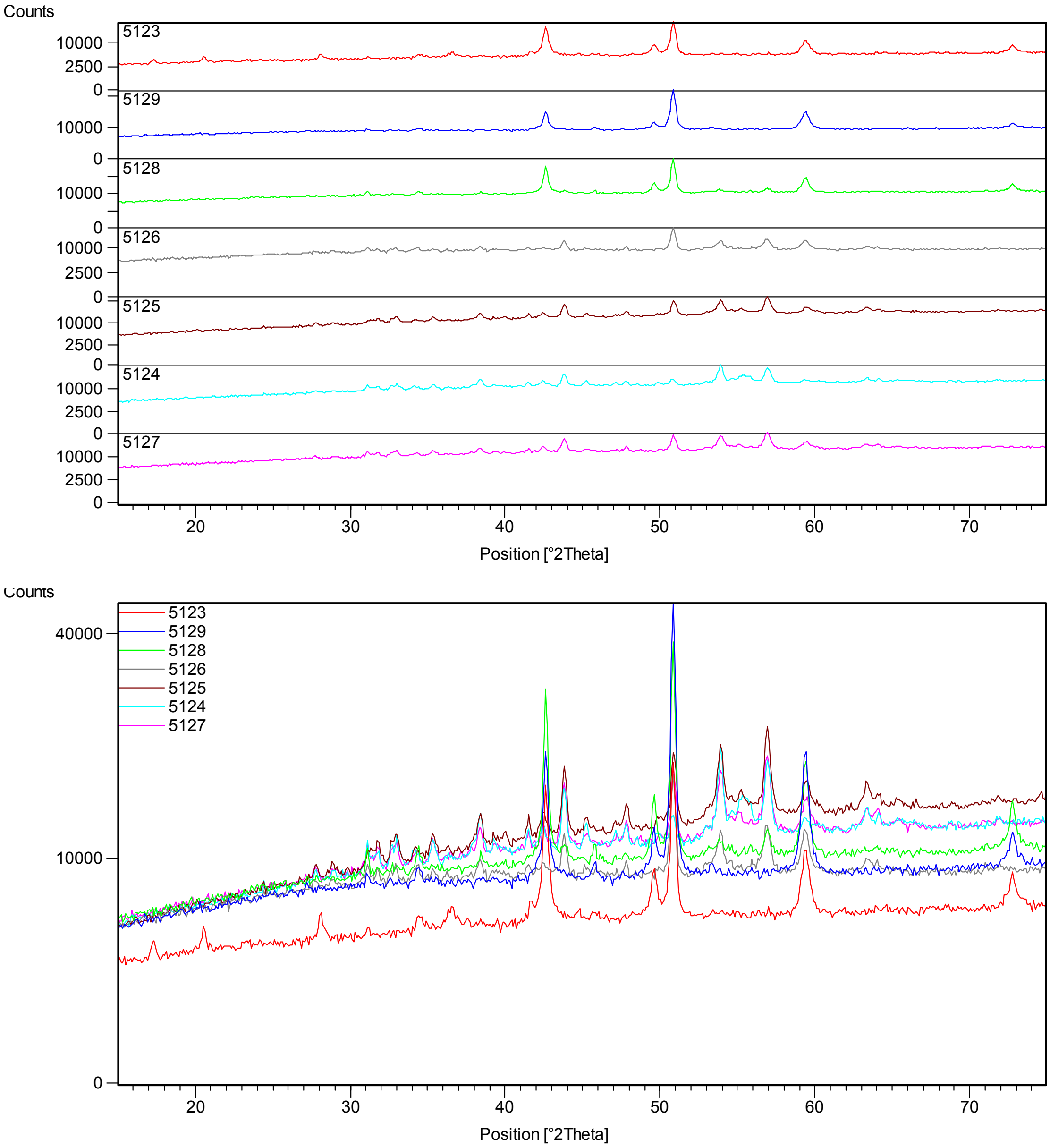
Table 16 Weight changes for the Cluster 2, 18 month samples (Rod 8)

Depth (m)	Sample No.	Weight(g) Before	Weight (g) After	Difference
0.5	68	46.94	46.95	0.01
0.7	48	47.15	47.14	-0.01
0.9	47	47.46	47.46	0
1.1	46	47.81	47.80	-0.01
1.3	45	47.01	47.02	0.01
1.5	44	46.84	46.75	-0.09
1.7	43	47.43	47.39	0.04



Cluster	Months burial	Rod	Depth (m)	XRD Scan
1	18	4	0.5	5119
			0.7	5120
			0.9	5121
			1.1	5122
			1.3	5130
			1.5	5131
			1.7	5135

Figure 18 Cluster 1 XRD spectra for copper samples: 18 months, depth 0.5 to 1.7m



Cluster	Months burial	Rod	Depth (m)	XRD scan
2	18	8	0.5	5123
			0.7	5129
			0.9	5128
			1.1	5126
			1.3	5125
			1.5	5124
			1.7	5127

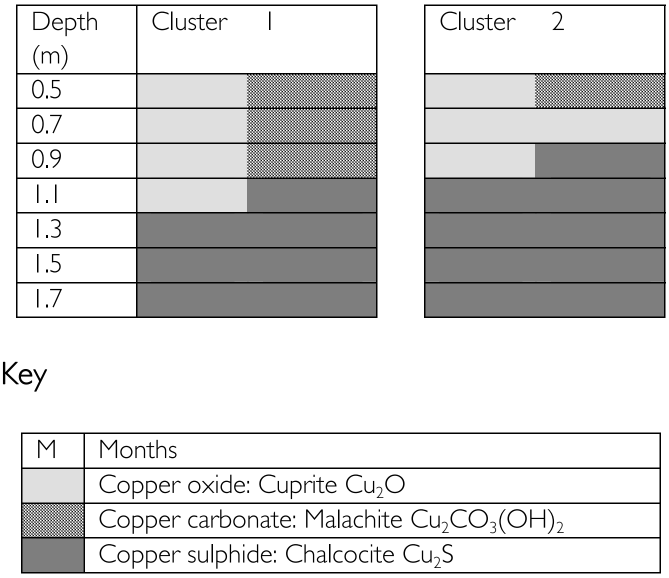
Figure 19 Cluster 2 XRD spectra for copper samples: 18 months, depth 0.5 to 1.7m

Table 17 Cluster 1, 18 month XRD analysis results

Depth (m)	Sample No.	XRD Scan	Major	Medium	Minor
0.5	64	5119	Copper	Malachite, Cuprite, Quartz	
0.7	24	5120	Copper	Malachite, Cuprite, Quartz	
0.9	23	5121	Cuprite, Malachite	Copper, Quartz	
1.1	22	5122	Copper	Chalcocite, Quartz	Cuprite
1.3	21	5130	Quartz	Copper, Chalcocite	
1.5	20	5131	Quartz, Copper	Chalcocite	
1.7	19	5135	Copper	Chalcocite, Quartz	

Table 18 Cluster 2, 18 month XRD analysis results

Depth (m)	Sample No.	XRD scan	Major	Medium	Minor
0.5	68	5123	Cuprite	Copper	Malachite
0.7	48	5129	Copper	Cuprite	
0.9	47	5128	Copper	Cuprite	Chalcocite, Quartz
1.1	46	5126	Copper, Chalcocite		
1.3	45	5125	Chalcocite	Copper	
1.5	44	5124	Chalcocite	Copper	
1.7	43	5127	Chalcocite	Copper	



Depth (m)	Cluster 1	
0.5	░	▒
0.7	░	▒
0.9	░	▒
1.1	░	■
1.3	■	■
1.5	■	■
1.7	■	■

Cluster 2	
░	▒
░	░
░	■
■	■
■	■
■	■
■	■

Key

M	Months
░	Copper oxide: Cuprite Cu_2O
▒	Copper carbonate: Malachite $Cu_2CO_3(OH)_2$
■	Copper sulphide: Chalcocite Cu_2S

Figure 20 Copper results for 18 months: major copper corrosion products identified through XRD analysis. The columns each represent a rod removed from cluster 1 or 2. The corrosion products are identified in the key, in some cases, two products occur at the same depth (i.e. cluster 1, depth 0.5m)

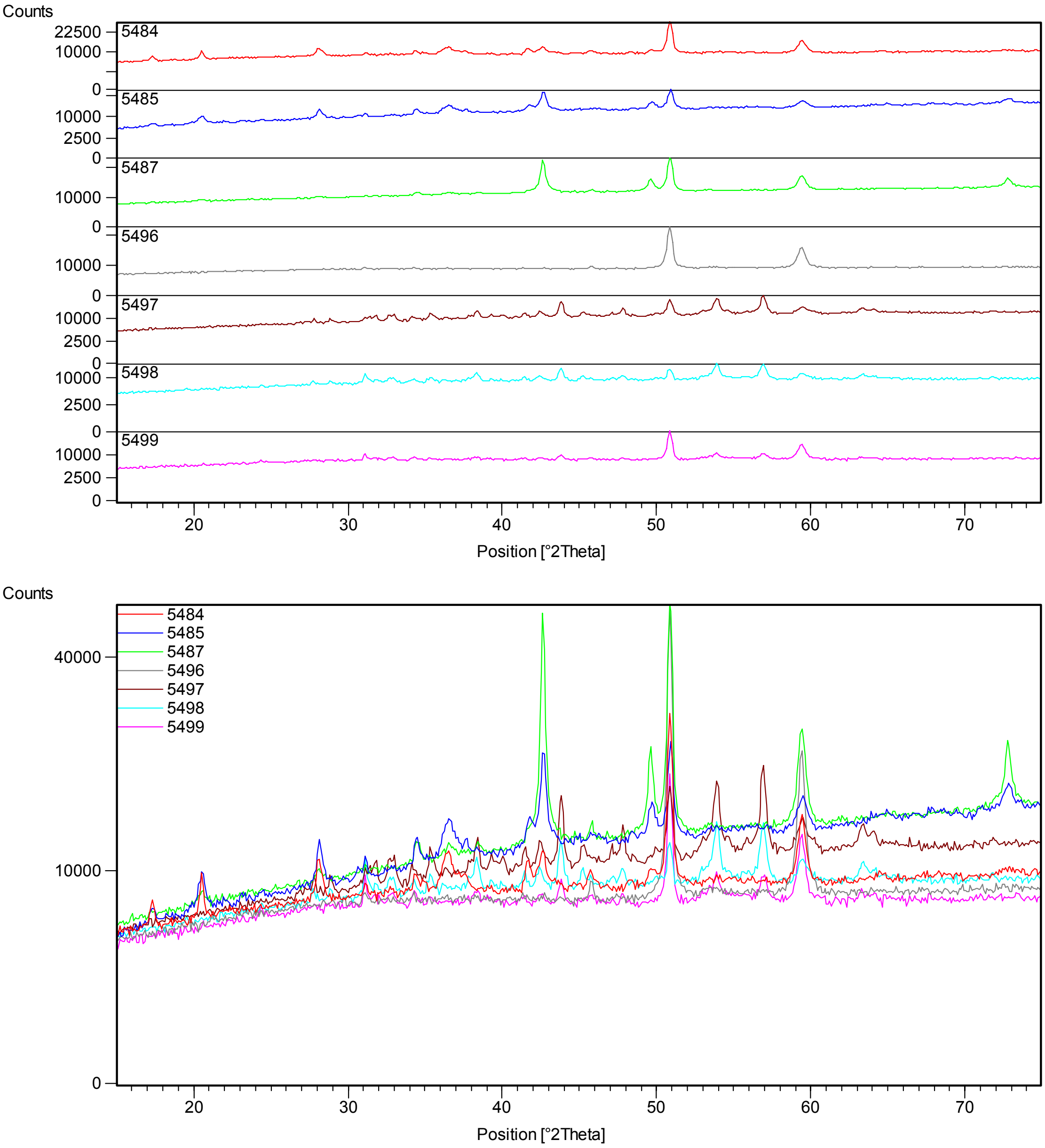
APPENDIX 4: 30 MONTH SAMPLES

Table 19 Weight changes for the Cluster 1, 30 month samples (Rods 3, 5 and 6)

Depth (m)	Rod no.	Sample No.	Weight(g) Before	Weight (g) After	Difference
0.5	3	63	46.56	46.57	0.01
	5	65	45.89	not taken	
	6	66	46.88	46.90	0.02
0.7	3	18	47.32	47.32	0
	5	30	47.61	not taken	
	6	36	47.75	47.75	0
0.9	3	17	46.80	46.76	-0.04
	5	29	47.30	47.26	-0.04
	6	35	46.51	46.48	-0.03
1.1	3	16	47.23	47.22	-0.01
	5	28	47.36	47.36	0
	6	34	45.96	45.92	-0.04
1.3	3	15	47.16	47.15	-0.01
	5	27	47.79	47.78	-0.01
	6	33	47.51	47.48	-0.03
1.5	3	14	46.85	46.84	-0.01
	5	26	47.77	47.75	-0.02
	6	32	46.10	46.10	0
1.7	3	13	46.02	46.01	-0.01
	5	25	47.51	47.48	-0.03
	6	31	47.39	47.36	-0.03

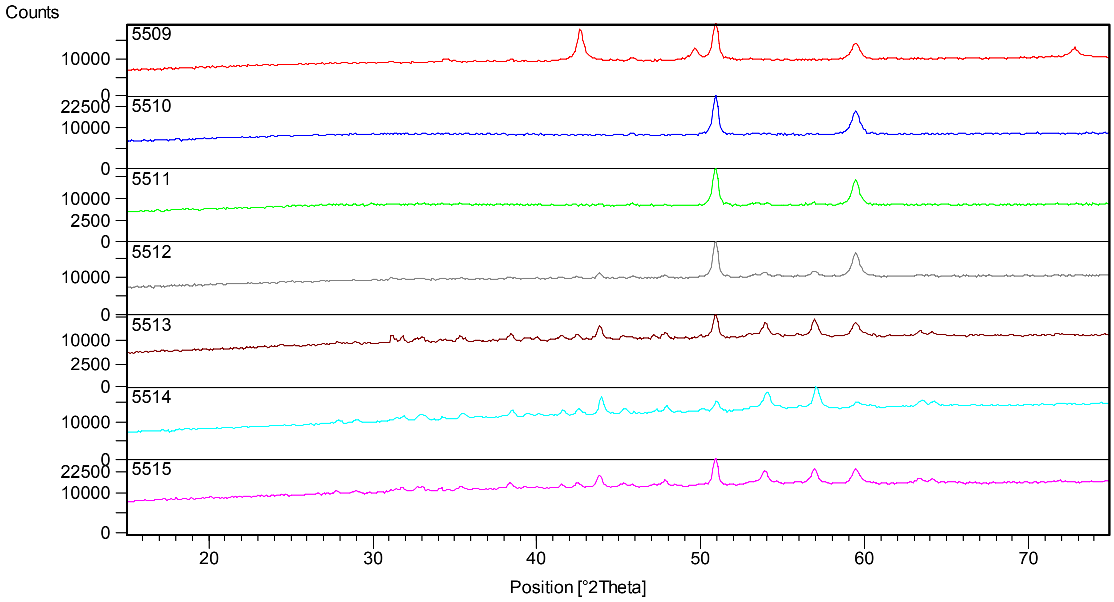
Table 20 Weight changes for the Cluster 2, 30 month samples (Rods 9 and 11)

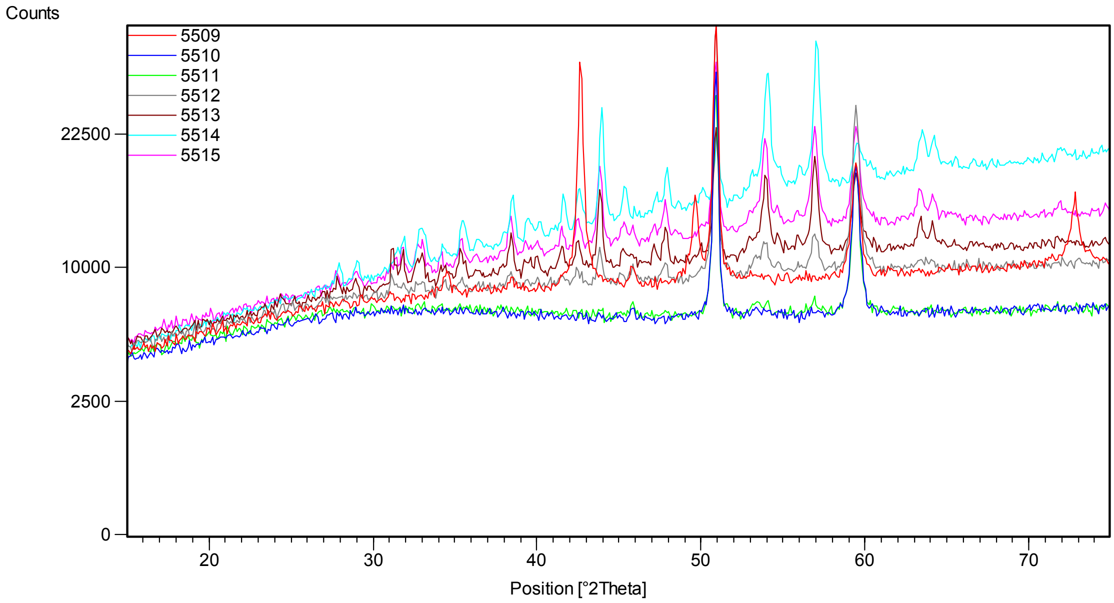
Depth (m)	Rod no.	Sample No.	Weight(g) Before	Weight (g) After	Difference
0.5	9	69	47.66	47.64	-0.02
0.7	9	54	47.29	47.27	-0.02
0.9	9	53	46.65	46.63	-0.02
1.1	9	52	45.98	45.88	-0.1
1.3	9	51	45.92	45.68	-0.24
1.5	9	50	46.86	46.62	-0.24
	11	72	47.09	46.66	-0.43
1.7	9	49	47.00	46.91	-0.09
	11	71	46.62		



Cluster	Months burial	Rod	Depth (m)	XRD Scan
1	30	6	0.5	5484
			0.7	5485
			0.9	5487
			1.1	5496
			1.3	5497
			1.5	5498
			1.7	5499

Figure 21 Cluster 1 XRD spectra for copper samples: 30 months, depth 0.5 to 1.7m





Cluster	Months burial	Rod	Depth (m)	XRD scan
2	30	9	0.5	5509
			0.7	5510
			0.9	5511
			1.1	5512
			1.3	5513
			1.5	5514
			1.7	5515

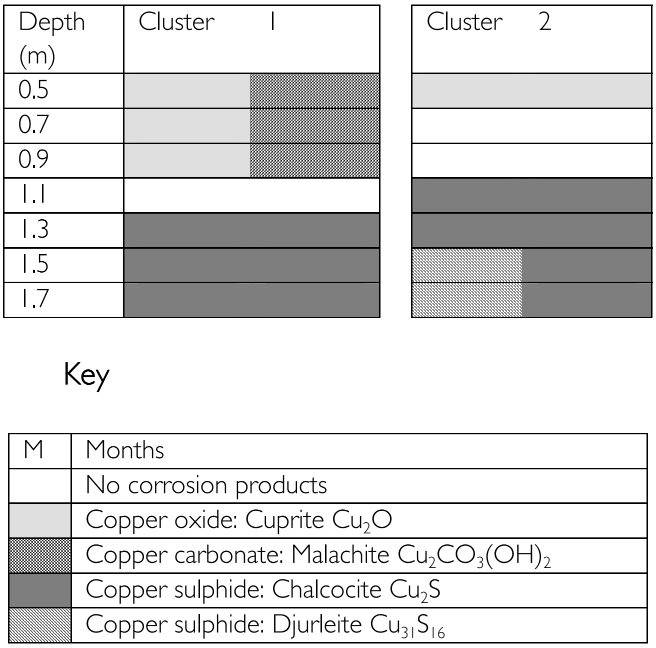
Figure 22 Cluster 2 XRD spectra for copper samples: 30 months, depth 0.5 to 1.7m

Table 21 Cluster 1, 30 month XRD analysis results

Depth (m)	Rod	Sample No.	XRD Scan	Major	Medium	Minor
0.5	3	63	5478	Copper	Malachite, Cuprite	
	5	65	5481	Copper	Malachite, Cuprite	
	6	66	5484	Copper	Malachite, Cuprite	
0.7	3	18	5479	Cuprite	Copper, Malachite	Quartz
	5	30	5482	Cuprite	Copper, Malachite	Quartz
	6	36	5485	Cuprite	Malachite, Copper, Quartz	
0.9	3	17	5480	Cuprite	Copper	Malachite
	5	29	5483	Cuprite, Copper	Malachite	
	6	35	5487	Cuprite, Copper	Malachite	
1.1	3	16	5488	Copper	Chalcocite	
	5	28	5492	Copper	Quartz, Calcite	Chalcocite
	6	34	5496	Copper		
1.3	3	15	5489	Copper	Chalcocite, Calcite, Quartz	
	5	27	5493	Copper	Chalcocite	
	6	33	5497	Chalcocite, Copper		
1.5	3	14	5490	Quartz, Chalcocite	Copper	
	5	26	5494	Quartz, Chalcocite	Copper	
	6	32	5498	Chalcocite	Copper	Quartz
1.7	3	13	5491	Quartz	Copper, Calcite	Chalcocite
	5	25	5495	Chalcocite	Quartz	
	6	31	5499	Copper, Chalcocite		Quartz

Table 22 Cluster 2, 30 month XRD analysis results

Depth (m)	Rod	Sample No.	XRD scan	Major	Medium	Minor
0.5	9	69	5509	Copper	Cuprite	
0.7	9	54	5510	Copper		
0.9	9	53	5511	Copper		
1.1	9	52	5512	Copper, Chalcocite		
1.3	9	51	5513	Chalcocite, Copper		
1.5	9	50	5514	Chalcocite	Copper	Djurleite
	11	72	5519	Cuprite	Copper	Djurleite
1.7	9	49	5515	Copper, Chalcocite		Djurleite
	11	71	5518	Cuprite	Copper	Djurleite



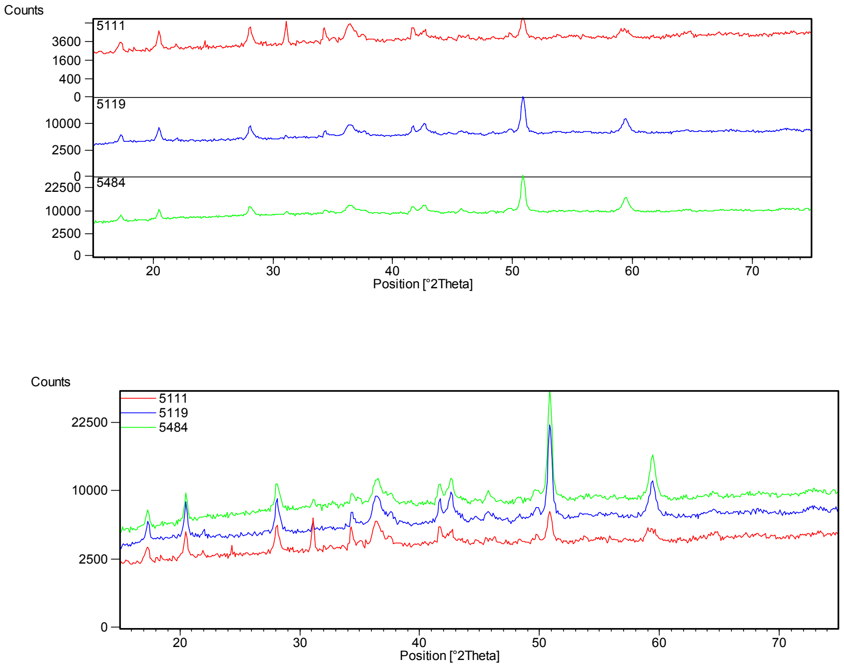
Depth (m)	Cluster 1	Cluster 2
0.5	░ ▓	░
0.7	░ ▓	
0.9	░ ▓	
1.1		■
1.3	■	■
1.5	■	▨ ■
1.7	■	▨ ■

Key

M	Months
	No corrosion products
░	Copper oxide: Cuprite Cu_2O
▓	Copper carbonate: Malachite $Cu_2CO_3(OH)_2$
■	Copper sulphide: Chalcocite Cu_2S
▨	Copper sulphide: Djurleite $Cu_{31}S_{16}$

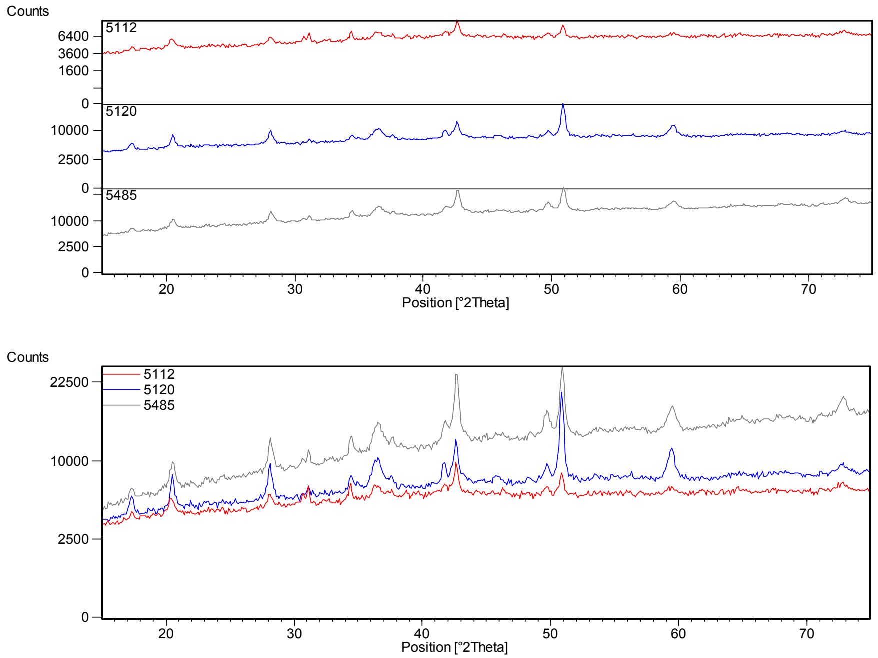
Figure 23 Copper results for 30 months: major copper corrosion products identified through XRD analysis. The columns each represent a rod removed from cluster 1 or 2. The corrosion products are identified in the key, in some cases, two products occur at the same depth (i.e. cluster 1, depth 0.5m)

APPENDIX 5: CLUSTER 1 RESULTS BY DEPTH



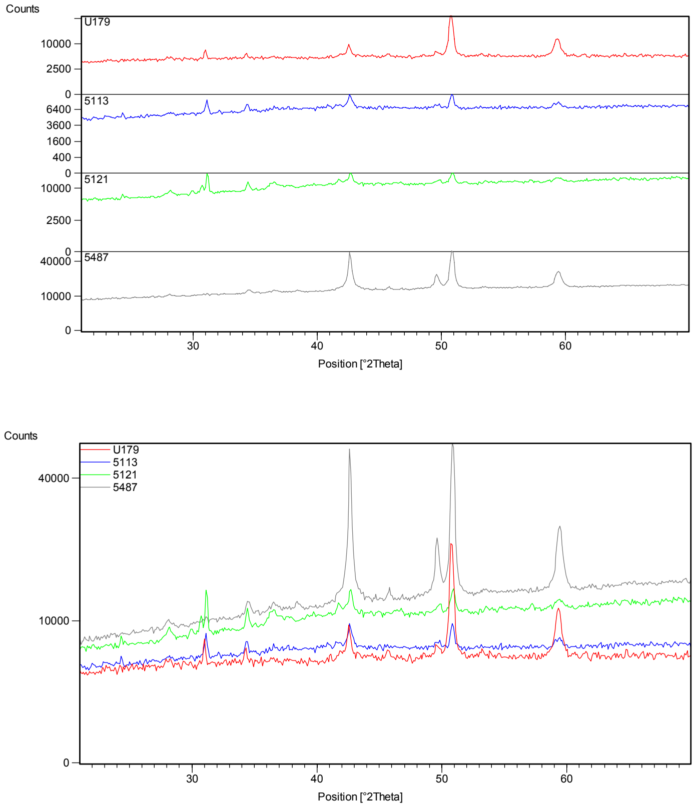
Cluster	Depth (m)	Months burial	Rod	XRD Scan
1	0.5	6	1	-
		12	2	5111
		18	4	5119
		30	6	5484

Figure 24 Cluster 1 XRD spectra for copper samples: depth 0.5m, 6 to 30 months



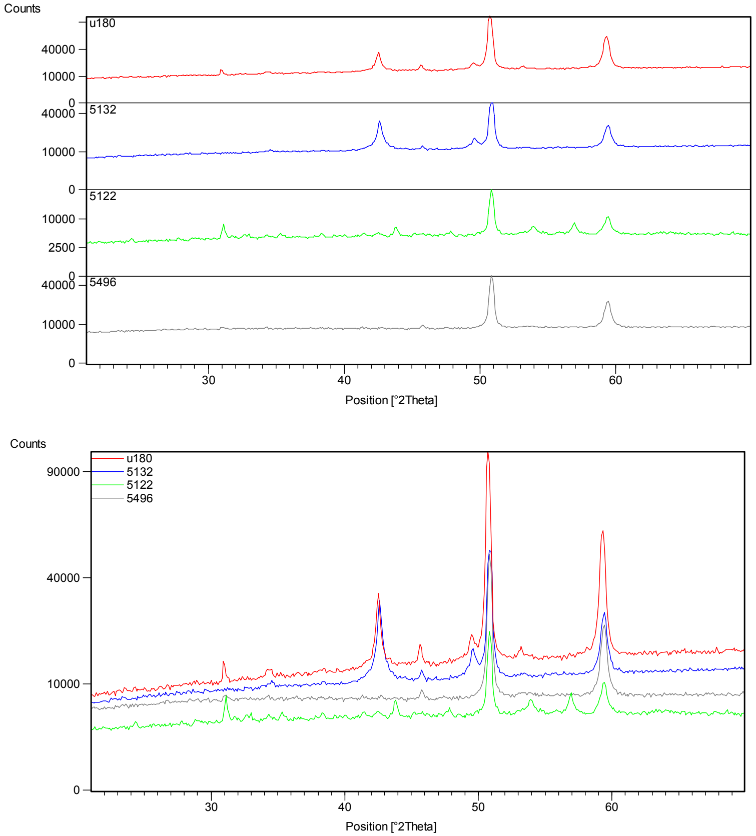
Cluster	Depth (m)	Months burial	Rod	XRD Scan
1	0.7	6	1	-
		12	2	5112
		18	4	5120
		30	6	5485

Figure 25 Cluster 1 XRD spectra for copper samples: depth 0.7m, 6 to 30 months



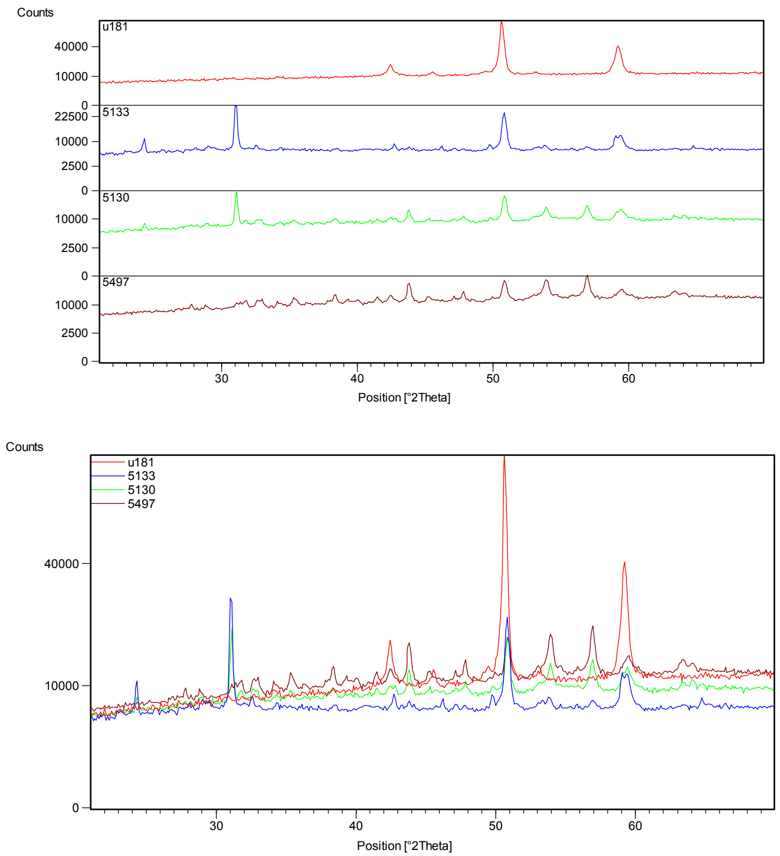
Cluster	Depth (m)	Months burial	Rod	XRD Scan
1	0.9	6	1	U179
		12	2	5113
		18	4	5121
		30	6	5487

Figure 26 Cluster 1 XRD spectra for copper samples: depth 0.9m, 6 to 30 months



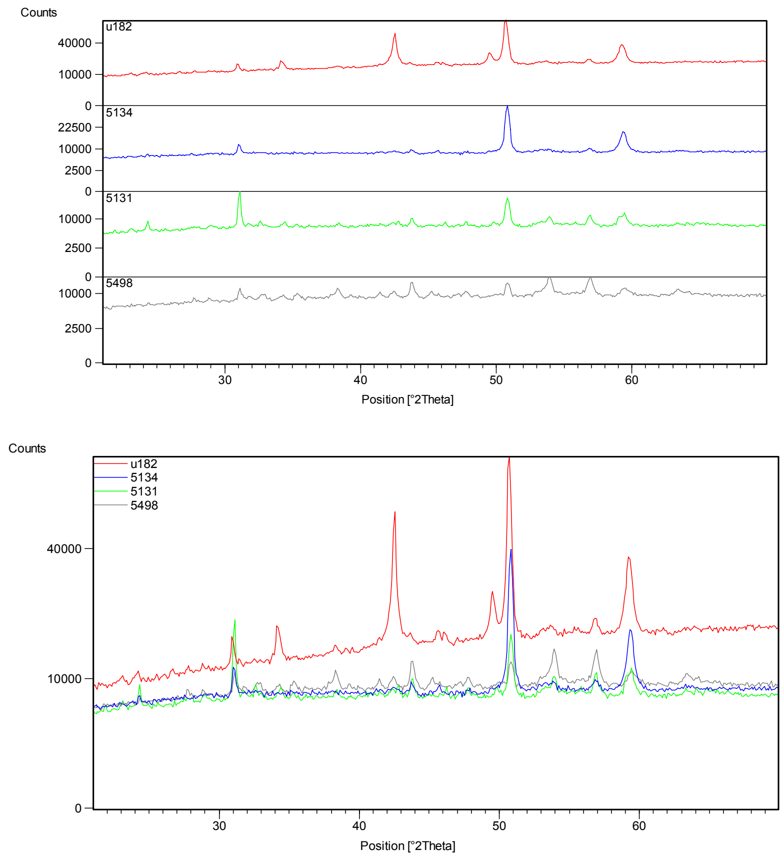
Cluster	Depth (m)	Months burial	Rod	XRD Scan
1	1.1	6	1	U180
		12	2	5132
		18	4	5122
		30	6	5496

Figure 27 Cluster 1 XRD spectra for copper samples: depth 1.1m, 6 to 30 months



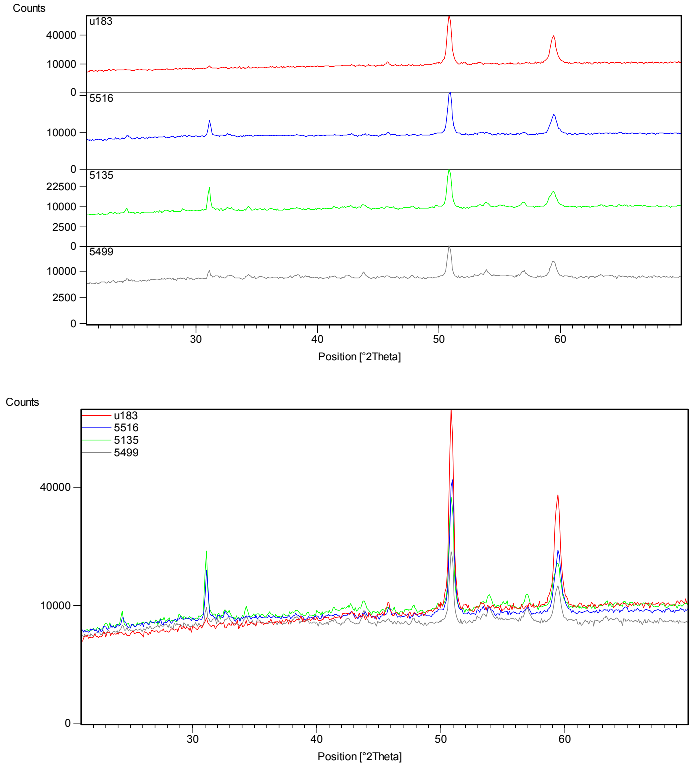
Cluster	Depth (m)	Months burial	Rod	XRD Scan
1	1.3	6	1	U181
		12	2	5133
		18	4	5130
		30	6	5497

Figure 28 Cluster 1 XRD spectra for copper samples: depth 1.3m, 6 to 30 months



Cluster	Depth (m)	Months burial	Rod	XRD Scan
1	1.5	6	1	U182
		12	2	5134
		18	4	5131
		30	6	5498

Figure 29 Cluster 1 XRD spectra for copper samples: depth 1.5m, 6 to 30 months



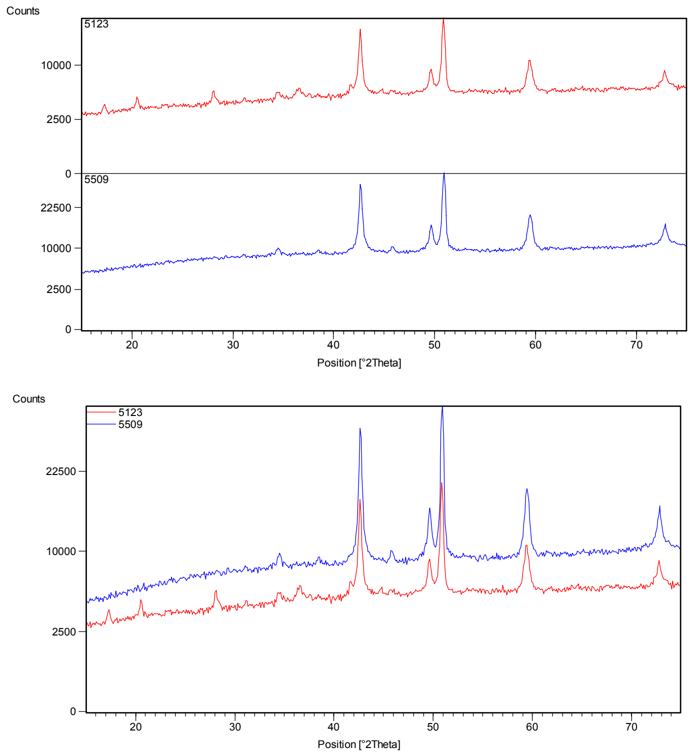
Cluster	Depth (m)	Months burial	Rod	XRD Scan
1	1.7	6	1	U183
		12	2	5516
		18	4	5135
		30	6	5499

Figure 30 Cluster 1 XRD spectra for copper samples: depth 1.7m, 6 to 30 months

Table 23 Cluster 1 major copper corrosion products identified through XRD analysis: 6 to 30 month results by depth

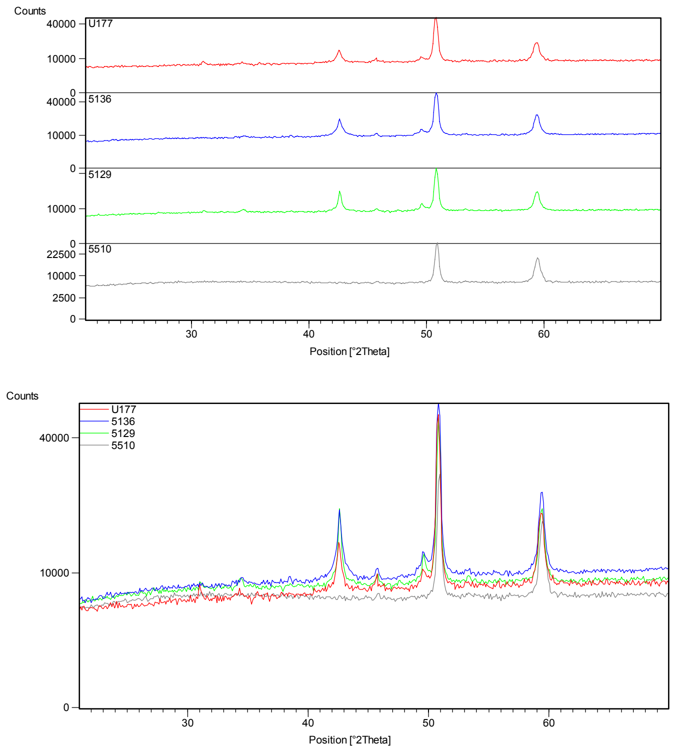
Depth (m)	Months Burial	Rod	Sample No.	Copper	Cuprite *Copper oxide*	Malachite *Copper carbonate hydroxide*	Chalcocite *Copper sulphide*	Quartz
0.5	6	1	61	Lost				
	12	2	62	▨	░	▩		▨
	18	4	64	▨	░	▩		▨
	30	6	66	▨	░	▩		
0.7	6	1	6	Lost				
	12	2	12	▨	░	▩		▨
	18	4	24	▨	░	▩		▨
	30	6	36	▨	░	▩		▨
0.9	6	1	5	▨	░			▨
	12	2	11	▨	░	▩		▨
	18	4	23	▨	░	▩		▨
	30	6	35	▨	░	▩		
1.1	6	1	4	▨	░			▨
	12	2	10	▨	░			
	18	4	22	▨	░		■	▨
	30	6	34	▨				
1.3	6	1	3	▨	░			
	12	2	9	▨			■	▨
	18	4	21	▨			■	▨
	30	6	33	▨			■	
1.5	6	1	2	▨	░		■	▨
	12	2	8	▨			■	▨
	18	4	20	▨			■	▨
	30	6	32	▨			■	▨
1.7	6	1	1	▨				
	12	2	7	▨			■	▨
	18	4	19	▨			■	▨
	30	6	31	▨			■	▨

APPENDIX 6: CLUSTER 2 RESULTS BY DEPTH



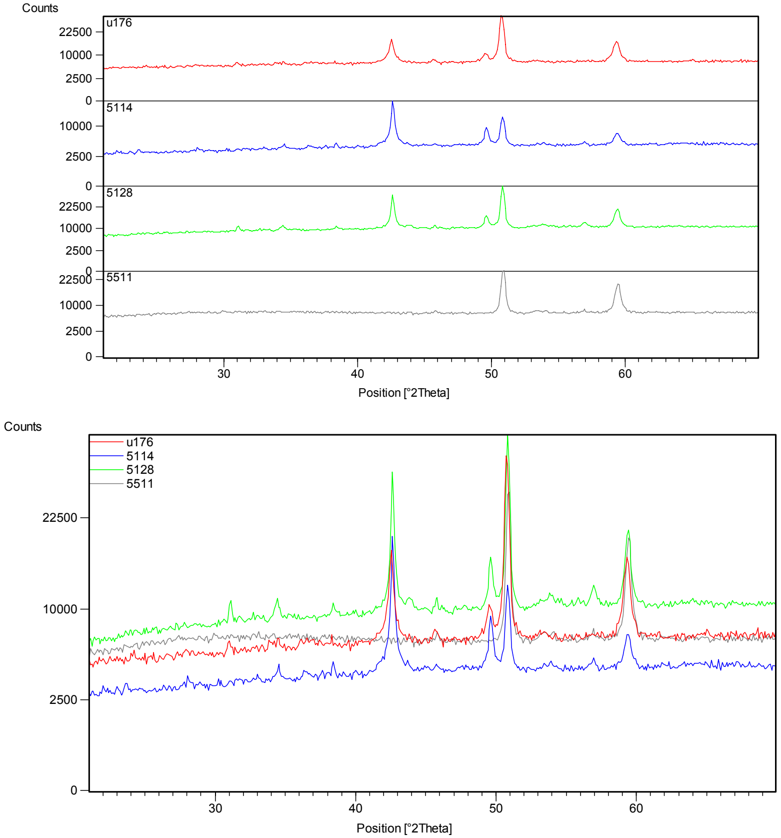
Cluster	Depth (m)	Months burial	Rod	XRD scan
2	0.5	6	7	–
		12	10	–
		18	8	5123
		30	9	5509

Figure 31 Cluster 2 XRD spectra for copper samples: depth 0.5m, 6 to 30 months



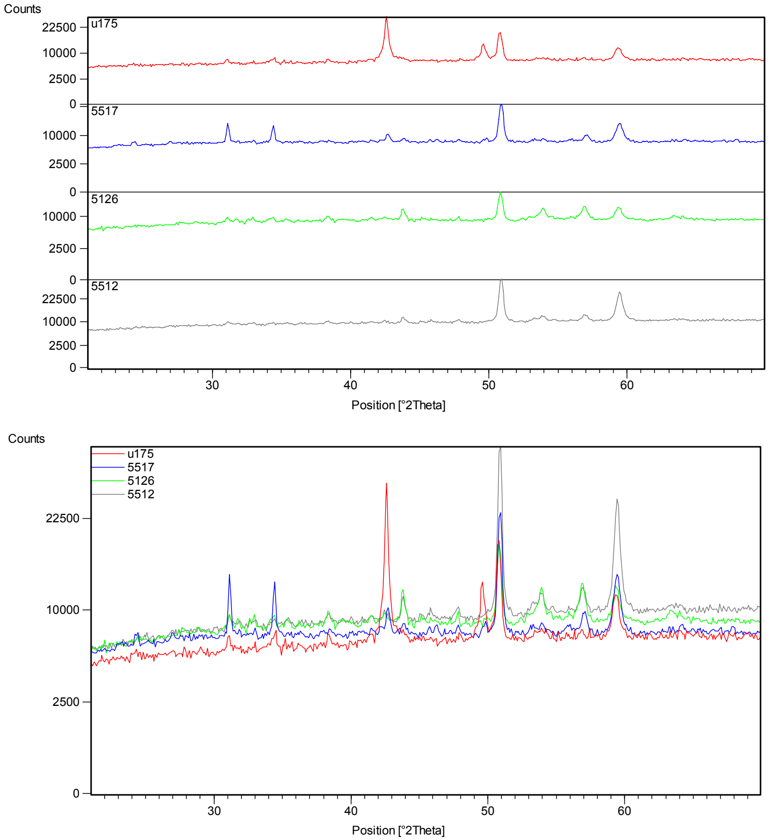
Cluster	Depth (m)	Months burial	Rod	XRD scan
2	0.7	6	7	U177
		12	10	5136
		18	8	5129
		30	9	5510

Figure 32 Cluster 2 XRD spectra for copper samples: depth 0.7m, 6 to 30 months



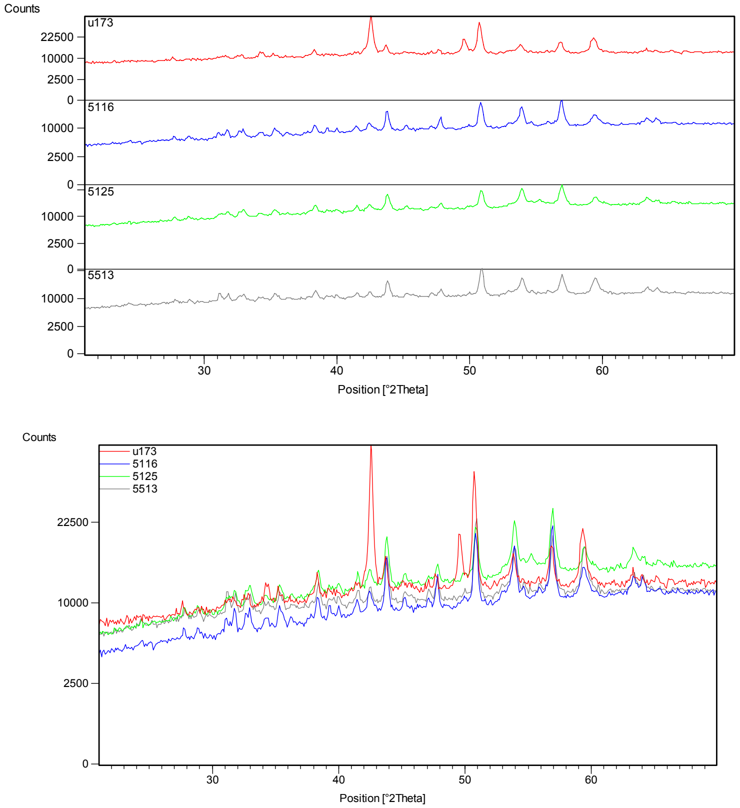
Cluster	Depth (m)	Months burial	Rod	XRD scan
2	0.9	6	7	U176
		12	10	5114
		18	8	5128
		30	9	5511

Figure 33 Cluster 2 XRD spectra for copper samples: depth 0.9m, 6 to 30 months



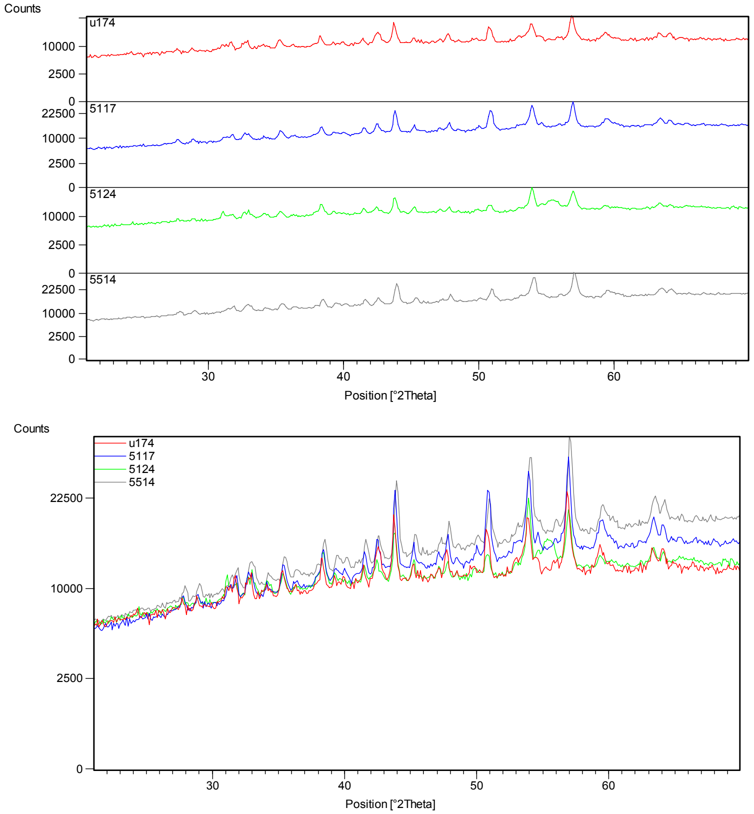
Cluster	Depth (m)	Months burial	Rod	XRD scan
2	1.1	6	7	U175
		12	10	5517
		18	8	5126
		30	9	5512

Figure 34 Cluster 2 XRD spectra for copper samples: depth 1.1m, 6 to 30 months



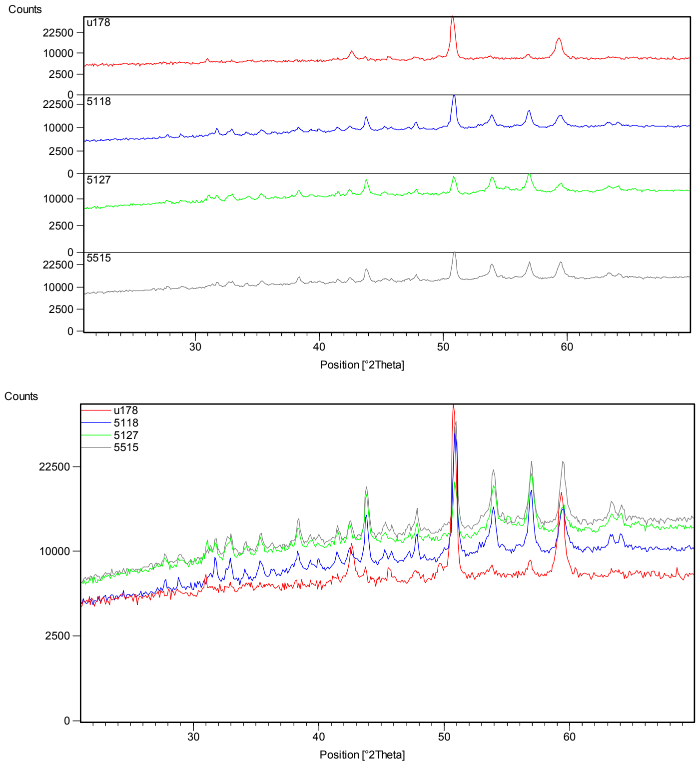
Cluster	Depth (m)	Months burial	Rod	XRD scan
2	1.3	6	7	U173
		12	10	5116
		18	8	5125
		30	9	5513

Figure 35 Cluster 2 XRD spectra for copper samples: depth 1.3m, 6 to 30 months



Cluster	Depth (m)	Months burial	Rod	XRD scan
2	1.5	6	7	U174
		12	10	5117
		18	8	5124
		30	9	5514

Figure 36 Cluster 2 XRD spectra for copper samples: depth 1.5m, 6 to 30 months



Cluster	Depth (m)	Months burial	Rod	XRD scan
2	1.7	6	7	U178
		12	10	5118
		18	8	5127
		30	9	5515

Figure 37 Cluster 2 XRD spectra for copper samples: depth 1.7m, 6 to 30 months

Table 24 Cluster 2 major copper corrosion products identified through XRD analysis: 6 to 30 month result

Depth (m)	Months Burial	Rod	Sample No.	Copper	Cuprite *Copper oxide*	Malachite *Copper carbonate hydroxide*	Chalcocite *Copper sulphide*	Djurleite *Copper sulphide*	Quartz
0.5	6	7	67	Lost					
	12	10	70	Lost					
	18	8	68	▨	░	▩			
	30	9	69	▨	░				
0.7	6	7	42	▨	░				▨
	12	10	60	▨	░				
	18	8	48	▨	░				
	30	9	54	▨					
0.9	6	7	41	▨	░				▨
	12	10	59	▨	░	▩			
	18	8	47	▨	░		▓		▨
	30	9	53	▨					
1.1	6	7	40	▨	░				
	12	10	58	▨	░				▨
	18	8	46	▨			▓		
	30	9	52	▨			▓		
1.3	6	7	39	▨	░		▓		
	12	10	57	▨			▓		
	18	8	45	▨			▓		
	30	9	51	▨			▓		
1.5	6	7	38	▨	░		▓		
	12	10	56	▨			▓		
	18	8	44	▨			▓		
	30	9	50	▨			▓	█	
1.7	6	7	37	▨	░		▓		▨
	12	10	55	▨			▓		
	18	8	43	▨			▓		
	30	9	49	▨			▓	█	

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