# Fiskerton: Scientific analysis of corrosion layers on archaeological iron artefacts and from experimental iron samples buried for up to 18 months

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#### Summary

In 2002 a project was set up to monitor the changes in condition of experimental modern materials placed in the vicinity of the Iron Age causeway at Fiskerton, Lincolnshire. This report describes the analytical methods and gives the results to date for the experimental iron samples, as well as the characterization of the corrosion products of twelve archaeological artefacts recovered during excavations and monitoring at Fiskerton in 1981, 2000 and 2001.

#### Keywords

Conservation, Iron Age, iron,

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# Introduction

The Iron Age wooden causeway at Fiskerton, Lincolnshire was excavated in part in 1981 (Field and Parker Pearson 2003) and 2001 (Field et al 2003). In 2001, the Witham Valley Research Committee was established to assess the survival and threats to the archaeology in the immediate vicinity of the causeway and in the wider area of the River Witham Valley (Catney and Start 2003; Last 2005). The causeway has been under fairly intensive arable farming and drainage regime for a number of years. Recent changes to land management have allowed water-tables to rise, which favour the creation of a natural wildlife habitat under a local Countryside Stewardship Scheme. However, the effects of raising the water levels on the already desiccated soil and the archaeological structures and artefacts are not known, and it is possible that this may be detrimental due to the introduction of different water chemistry and oxygen levels on site.

One of the projects to result from the Witham Valley Research Committee initiative was a conservation management project set up with the following aims:

- To assess the current state of preservation at the site
- To determine the impact of re-watering on the preservation of archaeological materials at Fiskerton
- To test methodologies for assessing the conditions of a variety of archaeological materials so that these methodologies could be used in the future at other sites in the Witham Valley and elsewhere
- To provide guidance on future management of archaeological material at Fiskerton.

To try to meet these aims, the project will assess the condition of previously excavated archaeological metalwork and the deterioration of a range of modern experimental samples buried in the vicinity of the causeway. Additionally, the groundwater levels and water quality are determined through a monthly monitoring programme arranged by Jim Williams, English Heritage Regional Science Advisor for the East Midlands. These measurements will include characteristics such as pH, redox potential, temperature and chemical composition through sampling at a number of points near the causeway.

The methods of burial and recovery of the modern experimental materials are described elsewhere by the researchers responsible for devising analytical programmes for each type of material (Fell et al 2005). The results from the experimental iron samples recovered at 6, 12 and 18 months burial durations are reported on here, together with the results from nine archaeological artefacts excavated in 1981, two artefacts recovered during monitoring in 2000, and one artefact recovered during a small excavation in 2001. The analytical results of the artefacts excavated in 1981 were incorporated in a paper presented at a conference in 1998 (Fell and Ward 1998) alongside samples of artefacts from other waterlogged sites, but it is useful to repeat the X-ray diffraction (XRD) results here to enable comparisons. The initial XRD results from the 6 month experimental iron and from three archaeological iron artefacts recovered in 2000-1 (Fig 1) were presented at a conference in 2004 (Fell and Williams 2004) and are given here also for comparison. All the results

presented in the present report will be discussed in greater depth and interpreted alongside the groundwater data at a later date when further data from the experimental iron are available. The purpose of the present report is principally to record the methods of analysis of the iron and to give the results determined so far.



Fig 1. The three artefacts recovered in 2000–1 which were sampled for analysis of corrosion products. Top left: shaft-hole axe-head 11 (length 262 mm). Top right: socketed lugged axe-head 131 (length 155mm). Lower: currency bar 10 (length 700mm)

# Methods

### Archaeological iron

The archaeological artefacts analysed are from anoxic peaty deposits from the vicinity of the Iron Age causeway. They are contemporary with the use of the causeway (from at least 457 to 321 BC) and are dated stylistically to the Iron Age (Field and Parker Pearson 2003).

The 1981 excavation was immediately north of the north delph of the River Witham whereas the 2001 excavation was just south of the north delph, between the north delph and the River Witham (Field and parker Pearson 2003; Field et al 2003, fig 4; J Rylatt forthcoming). The artefacts recovered in 2000 are from monitoring works on the river banks in the vicinity of Fiskerton, which is part of an on-going Environment Agency project to enhance the flood defences.

The selection of ferrous artefacts for analysis from the 1981 excavation was targeted towards those with corrosion layers that seemed likely to comprise iron sulphides (black or lustrous white deposits) because that particular study was to investigate the occurrence of iron sulphides on archaeological iron artefacts. The samples were selected at random as those that could be readily detached from the surfaces of the artefacts, although biased towards the underlying darker or lustrous deposits.

The selection of three artefacts for analysis from the ten ferrous items recovered during 2000 and 2001 was based on their robust condition and because they seemed to have been waterlogged probably continuously since burial. The three artefacts analysed (Fig 1) were a currency bar (2000 sf 10), a shaft-hole axe-head (2000 sf 11) and a socketed axe-head (2001 sf 131), each of which provided:

- Five samples of surface corrosion products for XRD analysis to determine the chemical compounds present. These were prepared and analysed according to standard methods, described later.
- One metallographic sample comprising a continuous corrosion layer from metal outwards, for the technological study of the metal (to be reported elsewhere) and for the study of corrosion products by scanning electron microscopy with energy-dispersive x-ray analysis, published elsewhere (Fell and Williams 2004).

#### **Experimental iron**

Samples of modern materials were buried at various depths, down to 2 metres, adjacent to the two clusters of groundwater monitoring peizometers nearest to the north delph of the River Witham (Clusters 1 and 2). Cluster 1, the more southerly group of peizometers and nearest the north delph, is less than 2m from the delph edge. Cluster 2 peizometers are c. 50m further away from Cluster 1 and from the River Witham, towards the modern village of Fiskerton. The methods of installation of the monitoring equipment is described elsewhere (Williams 2005).

The sample coupons of iron, mounted on a series of inert core rods, were installed on 22 December 2003. One installation rod of eight iron coupons (Fig 2) was recovered from both locations (Cluster 1 and Cluster 2) at intervals of 6 months (22 June 2004), 12 months (22 December 2004) and 18 months (22 June 2005). The coupons are referred to in this report by burial duration time, Rod number, and Bar number (eg 6 month, Rod 1, Bar 2). The approximate depths of the bars below ground level together with the soil types are shown in Table 1.

Once extracted from the ground (Figs 2–4), the six month coupons were initially stored wet and cool (the installation rod was wrapped in polythene sheet and stored refrigerated at 4°C). After several weeks, the coupons were photographed, dried with alcohol (rinsed with Industrial Methylated Spirits) and stored desiccated with silica gel. The twelve month coupons were treated differently: they were immediately dried on site and stored desiccated and anoxic until analysed (cf Graham 2005). Because of the uncertainty whether desiccation would alter the corrosion products during storage prior to XRD analysis, a test was performed with the 18 month coupons. Bars 1, 3, 5 and 7 of Rod I were stored wet and analysed within 48 hours of removal from the ground. These bars were then desiccated and re-analysed six weeks later and the results compared. The other bars (Bars 2, 4, 6, and 8 of Rod I, and all the bars of Rod 2) were all dried on site and stored desiccated and analysed.



Fig 2. Installation rod of iron samples as recovered after 6 months burial. The 8 bars or coupons of iron are between the white spacers. The 2 metre length of the installation rod is shown leaning against the fencing around Cluster 2 monitoring point.

The following analyses of the experimental iron bars are planned:

• Identification of the corrosion products by XRD analysis. Samples were selected to include the full thickness of the corrosion layers.

• Corrosion rate, as a measure of the weight of corrosion products generated per coupon over time (cf Matthiesen et al 2004)

• Characterization of corrosion type and comparison with samples from archaeological artefacts from Fiskerton.

#### X-ray diffraction analysis

X-ray diffraction analysis will detect only crystalline phases and therefore amorphous components will not be determined. Nevertheless, it is a standard analytical method for determining minerals and corrosion products on archaeological artefacts, as well as numerous other applications.

Samples in the order of 1mg were ground in an agate mortar and mounted on a flat single-crystal silicon sample holder, designed to reduce background scatter. Selected samples were stored wet until analysis and these were ground in the agate mortar with a few drops of alcohol (Industrial Methylated Spirit) and allowed to dry just prior to mounting on the sample holder.



Fig 3. Installation rods as recovered. Left: Rod 2 after 12 month burial showing the lowest four bars (Bars 1–4) covered with peaty soil. Right: Rod 2 after 6 months burial showing detail of Bars 6 and 7.

![](_page_8_Picture_2.jpeg)

Fig 4. Rod 1 Bar 8 in the laboratory just prior to removal from the installation rod for sampling for analysis. The 50mm bar (or coupon) of iron is held with nylon cable ties between the white spacers.

X-ray diffraction data were collected on a Philips PW 1840 powder diffractometer using cobalt K $\alpha$  radiation (wavelength K $\alpha$ 1 = 0.178896nm, K $\alpha$ 2 = 0.179285nm) incorporating a solid-state silicon detector. The running parameters were normally 40kV 40mA for X-ray generation. Data collection was normally between the angles 7 and 100°2 $\theta$  (or sometimes less, such as 10 – 90°2 $\theta$ ), at step size 0.10° per step, time per step 5s, with a receiving slit width of 0.3mm.

A search-match computer programme was used to identify unknown components in the diffraction patterns by comparison with standards in the powder diffraction file (International Centre for Diffraction Data, ICDD, powder diffraction files (PDF) version 1, based on ICPDS files). The raw data (.RD) files for all analyses are stored on the PW1840 computer and backup copies are made at intervals. Minerals named in this report, their formulae and their PDFs are shown in Table 2.

#### **Corrosion rates**

The original intention to determine corrosion rates has not yet been attempted for the following two reasons:

- 1) The amounts of corrosion products are relatively low and it would therefore be difficult to achieve meaningful results.
- 2) To determine the corrosion rates requires removal of all of the corrosion products in order to allow comparison of weight after burial and original weight. Although this will be done in the future, at present it is preferred to leave the corrosion products *in situ* on the bars, in case additional XRD analyses are required to check identifications of compounds.

### Results from the archaeological iron

The visual appearance of the samples analysed by XRD are described in Appendix 1. A concordance list for the results is given in Appendix 2.

Analytical results for the artefacts excavated in 1981 are summarised in Table 3 and selected spectra are shown in Appendix 3. Results for the artefacts recovered in 2000–1 are shown in Table 4 and the spectra are shown in Appendix 4.

Results from the artefacts excavated in 1981 (Table 3 and Appendix 3) show that the principal phases determined were siderite in six of the nine artefacts examined, and iron sulphides of various phases (pyrite, greigite and mackinawite) in five artefacts. Calcite was a minor component in three artefacts.

In the artefacts recovered in 2000–1 (Table 4 and Appendix 4), the dominant crystalline phases determined were greigite and siderite in all three artefacts examined. Greigite formed a major component of the crystalline phases in nine

of the fifteen samples, often in conjunction with siderite, although the latter was only a major component in six samples. Other components detected were pyrite, mackinawite, goethite, magnetite, vivianite, as well as small amounts of calcite and other soil constituents such as quartz.

# Results from the experimental iron

For each burial duration (6, 12, and 18 months), there are XRD analytical results for two rods, each comprising eight coupons of iron (in total 48 coupons). Because the soil conditions are different for the two burial locations, it is useful to compare the results through time for the two rods separately.

#### Rod 1 at 6, 12 and 18 months

The visual appearances of the bars are noted in Appendix 5 and selected examples are shown in Figures 5 and 6. The XRD results are summarised in Table 5. Appendix 6 provides a concordance list for the spectra shown by burial duration in Appendices 7–9.

![](_page_10_Picture_5.jpeg)

![](_page_10_Figure_6.jpeg)

The significant components detected by XRD for Rod 1 are:

At 6 months (Table 5, Appendix 7):

- The iron oxides goethite and lesser amounts of magnetite are the main components (Bars 3–8) (but see discussion later on magnetite and maghemite)
- The iron sulphide, greigite, on the lowest coupon (Bar 1)
- The iron oxide, lepidocrocite, on the highest coupon (Bar 8).

At 12 months (Table 5, Appendix 8):

- Principally goethite (Bars 1 and 4–8), with magnetite (Bars 6–8)
- The iron sulphide, mackinawite, on the second lowest coupon (Bar 2).

At 18 months (Table 5, Appendix 9):

- Goethite and magnetite (Bars 5–8)
- More greigite and at a wider range of depths (Bars 1– 5)
- Lepidocrocite on the upper three coupons (Bars 6–8)
- Small amounts of the iron carbonate, siderite, on Bars 1–5.

![](_page_11_Picture_8.jpeg)

Fig 6. Comparison of Rod 1 Bars 1, 3 and 8 at 18 month burial duration. Bar 1 (lower) shows typical orange-red accretions over black deposits. Bar 3 (centre) reveals a lustrous layer of relatively thin corrosion products. Bar 8 (top), also shown in Fig 5 top, has some bare metal plus thin orange and brown corrosion products. Lengths of bars c. 50mm.

#### Rod 2 at 6, 12 and 18 months

The visual appearances of the bars are noted in Appendix 5 and selected examples are shown in Figure 7. The XRD results are summarised in Table 6. Appendix 6 provides a concordance list for the specta shown in Appendices 10–12, and Figure 8 shows the spectrum of the commonest constituent siderite. The significant components detected by XRD for Rod 2 are:

At 6 months (Table 6, Appendix 10):

- Mainly goethite and magnetite on all coupons
- Mackinawite and greigite on Bars 2-4.

#### At 12 months (Table 6, Appendix 11):

- Siderite on all the coupons except the uppermost (Bars 1–7, see Fig 8)
- Goethite and magnetite (Bars 6–8)
- Greigite (Bars 2 and 3).

#### At 18 months (Table 6, Appendix 12):

• Siderite on all coupons (Bars 1–8)

- Greigite on Bars 1, 2, 6 and possibly 5
- Lepidocrocite on Bars 3 and 4
- Goethite on Bars 6–8 and possibly 5.

![](_page_12_Picture_3.jpeg)

Fig. 7. Bars 1, 2 and 5 of Rod 2 at 18 months burial duration. Lengths of bars c. 50mm.

![](_page_12_Figure_5.jpeg)

Figure 8. XRD spectrum for 12 month Rod 2 Bar 5 showing only siderite.

#### Effects of wet and dry storage (Table 5, Appendix 13)

The effects of wet storage (after recovery but before XRD analysis) compared with dry storage were investigated in Rod I, Bars 1, 3, 5 and 7, at 18 month duration. These coupons were initially stored wet and analysed by XRD within 48 hours after recovery, before being dried and re-analysed 6 weeks later.

There were a few very minor differences between the samples. Spectra for Bars 1 and 5 in both conditions appear to be the same. The dried Bar 3 (XRD Sample 5090) revealed three additional peaks (Fig 9):

Peak Á	Angle °2θ	27.964	'd' value (nm)	0.370205
Peak B	"	31.072	"	0.333954
Peak C	"	34.993	"	0.297516

The attribution for these peaks is probably:

Peak A	Dolomite, ferroan	Ca(Mg.Fe)(CO <sub>3</sub> ) <sub>2</sub>	(PDF: 34-0517)
Peak B	Quartz	SiO <sub>2</sub>	(PDF: 31-1233)
Peak C	Greigite	Fe <sub>3</sub> S <sub>4</sub>	(PDF: 16-0713)

The dried Bar 7 (XRD Sample 5088) revealed an additional small peak at angle 30.992 °20, 'd' value 3.34797, possibly attributable to carbon (PDF 26-1076) or graphite (25-0284), or just conceivably iron phosphorus nitride  $Fe_4P_6N_{12}S$  (PDF: 42-0652). These constituents, and also the dolomite above, may be an effect of drying of the soil matrix, whereas the quartz and greigite are detectable in most of this series of samples.

![](_page_13_Figure_7.jpeg)

Fig. 9. XRD spectrum showing the 3 peaks which appeared after drying 18 month Rod 1 Bar 3. The peaks occur at 27.964, 31.072, and 34.993°2 $\theta$  and are determined as dolomite ferroan, quartz, and greigite respectively.

#### Magnetite versus maghemite

Some XRD spectra were interpreted by the database to contain maghemite  $(\gamma$ -Fe<sub>2</sub>O<sub>3</sub>), for example Bars 7 and 8 of Rod 2 experimental iron at 12 months, as well as some of the archaeological samples from 2000-1. However, the XRD spectra for maghemite and magnetite are virtually identical and are better distinguished by thermal analysis or Raman spectroscopy (Cornell and Schwertmann 2003).

Magnetite is a common corrosion product, often formed by oxidation of a ferrous (Fe<sub>II</sub>) solution. Maghemite has a similar structure to magnetite except that all or most of the Fe is trivalent. At ambient conditions it can form through the oxidation of magnetite. Maghemite has seldom been reported as a natural corrosion product (but note Knight 1982, and Matthiesen et al forthcoming) although it is always possibly, if present, that it has formed as a consequence of the drying and extraction procedure prior to analysis.

To test for the presence of maghemite, the corrosion products from two experimental bars (12 months Rod I Bar 3, and 12 months Rod 2 Bar 7) determined as containing maghemite were spiked with standard reference maghemite (supplied by Alfa Aesar, and kindly donated by David Thickett). Re-analysis confirmed that the peaks in the experimental iron samples did match maghemite (PDF 39-1346). However, because of the similarity of the spectra of magnetite (PDF 19-0629) and maghemite, this exercise did not confirm the identity of the peaks. At present, this matter remains unresolved, and although not central to the aims or outcome of the analytical project, the topic has relevance and may be revisited in the future, particularly if other analytical facilities become available.

# Discussion

The analytical results are discussed only briefly here although they will be more fully interpreted elsewhere, together with the groundwater data, after additional experimental coupons have been evaluated.

#### Archaeological iron

Samples of corrosion layers from the archaeological artefacts yielded principally iron carbonate (siderite) and iron sulphides (greigite, mackinawite, pyrite), plus lesser phases comprising iron oxides (goethite, magnetite), iron phosphate (vivianite), and soil and other components such as calcite and quartz. The presence of these components has been discussed previously (Fell and Ward 1998; Fell and Williams 2004). In particular, the presence of siderite has been noted and compared with the occurrence also at Nydam Mose in Denmark, where siderite is also found as a major corrosion product on archaeological ironwork (Matthiesen et al 2003; Matthiesen et al forthcoming). The authors offer several possible explanations for its formation at Nydam Mose. At Fiskerton, its formation may not be through the same pathway because the ground water and soil conditions are different, as noted previously (Fell and

Williams 2004). Calcium carbonate, however, is often associated with sulphide production through the reduction of organic matter (cf Watson 1981). Thus the presence of both calcite and siderite on the artefacts from Fiskerton may be a by-product of this metabolic pathway. Obviously interpretations of the soil and water chemistry are required before full explanations can be offered.

The corrosion layers on the archaeological artefacts recovered to date are often very thin, presumably a consequence of little active corrosion of the artefacts in the waterlogged burial environment. The presence of remanent microstructures surviving in the corrosion layers (Fell 2003) is not uncommon in less corroded iron artefacts such as those from anoxic environments at near neutral pH.

#### **Experimental iron**

The experimental coupons at Cluster 1 (Rod I) are placed very near to the north delph of the River Witham and as such they are susceptible to constant changes in the water levels in the delph. For example, levels are altered by flushing of the dykes and by clearance of the dykes in the area by the Internal Drainage Board. In the Autumn of 2004, the water-table was deliberately raised by the blocking of the land drainage ditches by the farmer. By mid-November, the water levels at Cluster 1 had raised slightly, to an average depth of 0.9m from the soil surface compared with previous levels of between 1.0m and 1.5m depth (J Williams pers comm). Measurements of redox potential and pH have remained in the neutral range.

Coupons at Cluster 2 (Rod 2), placed 50m further away from the north delph could be expected to be less oxic than Rod 1, particularly in the lower depths of soil where anoxic conditions should prevail. The water levels here are now around 0.3m to 0.6m depth from the surface and are more consistent than the previous levels which ranged from 0.7m to 1.6m depth (J Williams pers comm).

The experimental coupons at 6 months burial have yielded mainly oxides, probably due at least in part to oxygen being taken down into the soil with the coupons at their installation. At 12 and 18 months, the corrosion layers are becoming increasingly like those on the archaeological ironwork, comprising mainly siderite and iron sulphides. This is much more noticeable for the Rod 2 coupons, most probably because the water levels are higher and more consistent than those near to the river and delph. For example, at 12 months burial, the iron coupons which are 1.2m below ground at Cluster 2 (Rod 2, Bars 1–5) show consistently siderite, whereas 1.0m and above (Bars 6–8) yield the iron oxyhydroxide, goethite. It is worth noting that the 12 month burial duration occurs about a month or so after the raised groundwater levels achieved relatively uniform measurements. At 18 months burial duration, siderite is the commonest corrosion product on the iron coupons at Cluster 2, occurring on all eight coupons, whereas it is rare at Cluster 1, where goethite dominates.

#### The impact of re-watering at Fiskerton

The predominance of siderite on the experimental iron coupons which are now waterlogged, as well as on the archaeological artefacts, will require further

consideration. Siderite as a corrosion product is considered to confer stability to artefacts through its passivating properties (Matthiesen et al 2003). At Fiskerton, the conclusions to date from the analyses described in this report suggest that the re-watering of the site may be beneficial to the archaeological iron due to the presence of siderite and the continuation of, or at least re-introduction of, anoxic and waterlogged conditions.

#### Future work

1. There will be further recoveries of experimental iron coupons. At both burial locations, there are three more rods of coupons, and the next probable recovery will be in June 2006 at the 2.5 year burial anniversary.

2. As indicated above, data from the groundwater measurements requires thorough interrogation and the analytical results from the experimental iron coupons will then be interpreted more fully.

3. The effects of wet storage compared with dry storage of the coupons have been investigated briefly and there appears to be little advantage to dry the coupons on site providing that analysis will occur within a short timescale. However, this topic would benefit from further research to inform future potential burial experiments in the Witham Valley and elsewhere.

4. XRD analysis will not detect amorphous compounds, nor distinguish between the corrosion products magnetite and maghemite. Opportunities to resolve these problems will be sought.

### Acknowledgements

I thank Malcolm Ward for XRD analysis of the samples from artefacts excavated in 1981 and for his illustrations as used for Figure 1 and Appendix 3. Roger Wilkes has patiently nudged the XRD analyser into action on numerous occasions over the last three years and without which the analyses could not have been completed. David Thickett kindly supplied a reference sample of maghemite.

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Bar	Depth (m) *	Depth range (m) **	Cluster 1 / Rod 1 Soil type	Cluster 2 / Rod 2 Soil type
1	1.61	1.59–1.74	Reedy silt	Reedy silt
2	1.58	1.56–1.61	Reedy silt	Reedy silt
3	1.45	1.43–1.48	Reedy silt	Reasonably well
			-	preserved peat
4	1.32	1.30–1.35	Reedy silt	Reasonably well
				preserved peat
5	1.19	1.17–1.22	Top of reedy silt	Reasonably well
				preserved peat
6	0.98	0.96–1.01	Degraded woody peat	Reasonably well
				preserved peat
7	0.77	0.75–0.80	Degraded woody peat	Degraded woody peat
8	0.56	0.54-0.59	Shelly silt	Degraded woody peat
* ^		مرجعين وجاوا والمتعر والمطالعين	halaw anawal (matura)	

Table 1. Depths of experimental coupons and soil types

\* Approximate depth to mid coupon below ground (metres)
\*\* Actual depths for the full lengths of the bars

Table 2. Corrosic	n products and	l other minerals	detected by XRD

Mineral name	Formula	PDF (ICDD)
Goethite	α-FeOOH	29-0713
Magnetite	Fe <sub>3</sub> O <sub>4</sub>	19-0629
Maghemite	γ-Fe <sub>2</sub> O <sub>3</sub>	39-1346
Siderite	FeCO <sub>3</sub>	29-0696
Lepidocrocite	γ-FeOOH	44-1415
Akaganeite	β-FeOOH	34-1266
Greigite	Fe <sub>3</sub> S <sub>4</sub>	16-0713
Mackinawite	Fe <sub>1+x</sub> S	24-0073 15-0037
Pyrite	FeS <sub>2</sub>	42-1340
Vivianite	$Fe_{3}(PO_{4})_{2}.8H_{2}O$	30-0662
Iron sulphide	FeS	23-1120
Calcite	CaCO <sub>3</sub>	05-0586
Quartz	SiO <sub>2</sub>	31-1233 33-1161

Table 3. XRD summary results for the archaeological iron artefacts excavated in 1981 (after Fell and Ward 1998)

	Crystalline components detected		
Object	Major	Minor	Trace
File 171	pyrite		
Rod 267	siderite	goethite	
Saw 288	siderite		unknown phase
Rod 312 B	siderite	goethite	
Axe 331	pyrite, greigite	calcite	
Hammer 332	siderite		
Axe 383	calcite	greigite	pyrite
Hammer 403	mackinawite		calcite
	siderite*		
Axe 413	siderite, greigite		

\* displaced to larger 'd' spacings

Table 4. XRD summary results for the archaeological iron artefacts recovered in 2000–1

		Crysta	alline components det	tected
S	Object	Major	Minor	Trace
1	Bar 10	greigite		siderite calcite
2	Bar 10	greigite calcite		
3	Bar 10	vivianite calcite	siderite	?goethite
				?magnetite
4	Bar 10	calcite siderite		greigite pyrite ?magnetite
5	Bar 10			areigite goethite
Ū	Durre			siderite + other
6	Axe 11	greigite		siderite calcite
7	Axe 11	greigite	magnetite	
8	Axe 11	greigite		calcite
9	Axe 11	greigite siderite		
10	Axe 11	siderite	greigite, magnetite goethite	
11	Axe 131	greigite siderite pyrite	-	
12	Axe 131	greigite siderite pyrite		?mackinawite
13	Axe 131		goethite, calcite, magnetite, quartz	
14	Axe 131	greigite siderite	pyrite	
15	Axe 131	pyrite	vivianite calcite	goethite

		Crystalline components detected		
Rod	Bar	Major	Minor	Trace
6 moi	nth buri	al duration Rod 1		
1	1	quartz, calcite	greigite	
1	2	quartz	calcite	
1	3	quartz, calcite	goethite	magnetite*
1	4	goethite, calcite		
1	5	goethite		magnetite
1	6	quartz, calcite	goethite	magnetite
1	7	quartz		goethite
1	8	goethite, lepidocrocite	magnetite	quartz
12 m	onth bur	ial duration Rod 1		
1	1	quartz		goethite
1	2	quartz	mackinawite	
1	3	quartz		?maghemite
1	4	goethite	quartz	
1	5	goethite		
1	6	goethite, calcite		magnetite
1	7	goethite, magnetite	calcite	
1	8	goethite,	calcite	
		magnetite		
10 m/	anth huu	ial duration . Rad 1		
10 110				2eidorito
1	2		aroiaito	
1	2	qualiz	greigite	2 Sidenie
1	5		qualiz, greigite, iron	oulei
1	Δ	acethite	mackinawite quartz	
1	7	goetinie	siderite	
1	5	aoethite	siderite areiaite	magnetite* other
1	6	goethite	calcite	
	Ũ	magnetite*		?lepidocrocite
1	7	goethite	calcite, magnetite*	other **
1	8	goethite	calcite, quartz	lepidocrocite
-	-	9	magnetite*	other
			<b>v</b>	
Wet v	. dry sto	orage (18 month Roc	1 only)	
1	1	No differences		
1	3	After drying, 3 peal	ks appeared, attributable	to: quartz, greigite,
		and dolomite ferroa	an (Ca(Mg.Fe)(CO <sub>3</sub> ) <sub>2</sub> ). S	See text
1	5	No differences		
1	7	After drying, a sing See text	le peak appeared possib	ly carbon or graphite.

Table 5. XRD summary results for the experimental iron coupons, Rod 1

\* Possibly maghemite, \*\* see results comparing wet and dry storage

	Crystalline components detected			
Rod	Bar	Major	Minor	Trace
6 mor	nth buria	al duration Rod 2		
2	1	maghemite*	-	-
2	2	goethite,	greigite	
		mackinawite,		
		calcite		
2	3	mackinawite,	calcite	magnetite*
		greigite		
2	4	mackinawite,	goethite	magnetite
		calcite		
2	5	goethite, calcite		
2	6	goethite	quartz	
2	7	goethite	calcite, quartz	
2	8	goethite,	quartz	calcite (+ some
		maghemite*		unknown peaks)
12 mc	onth bur	ial duration Rod 2		
2	1	siderite		quartz/calcite
2	2	siderite		greigite, quartz/calcite
2	3	siderite		greigite, quartz/calcite
2	4	siderite		
2	5	siderite		
2	6	goethite		siderite, magnetite?
2	7	goethite	calcite	siderite, magnetite*
2	8	goethite, calcite		magnetite*
18 mc	onth bur	ial duration Rod 2		
2	1	quartz, greigite	siderite	
2	2	siderite	quartz	greigite, other,
_	<u> </u>			magnetite*
2	3†	siderite, quartz	calcite, lepidocrite	other
2	4†		quartz, goethite,	magnetite*
L	_		?lepidocrite,	other
2	5	siderite		?goethite
2	6	siderite, calcite	greigite	goethite
2	7	siderite, calcite	goethite, ?greigite	
			magnetite*	
2	8	calcite	goethite,	siderite, quartz
			magnetite*	

# Table 6. XRD summary results for the experimental iron coupons, Rod 2

† = poor traces; \* Possibly maghemite

# Appendices

- 1. Visual appearance of the XRD samples from the archaeological artefacts
- 2. Concordance for the XRD results from the archaeological artefacts
- 3. XRD spectra for the archaeological iron artefacts excavated in 1981
- 4. XRD spectra for the archaeological iron artefacts recovered in 2000 and 2001
- 5. Visual appearances of the recovered experimental iron bars
- 6. Concordance for the XRD results for the experimental iron samples
- 7. XRD spectra for the experimental iron samples, 6 months, Rod 1, Bars 1–8
- 8. XRD spectra for the experimental iron samples, 12 months, Rod 1, Bars 1–8
- 9. XRD spectra for the experimental iron samples, 18 months, Rod 1, Bars 1-8
- 10. XRD spectra for the experimental iron samples, 6 months, Rod 2, Bars 1–8
- 11. XRD spectra for the experimental iron samples, 12 month, Rod 2, Bars 1–8
- 12. XRD spectra for the experimental iron samples, 18 month, Rod 2, Bars 1–8

13. XRD spectra for the experimental iron samples, comparing wet and dry storage conditions for Bars 1, 3, 5 and 7 from Rod 1, 18 month burial duration

# Appendix 1. Visual appearance of the XRD samples from the archaeological artefacts

No.	Object	Description of sample for XRD
4004 5		
1981 E	Excavation	Lustraus white L block dependence
	Pile 171 Bod frog 267	Orange, plug black deposite
	Rou llag 207	Orange, plus black deposits
	Dod frog 212 P	Orange, plus black deposits
	Avo 331	Lustrous white + black deposits
	Hammer 332	
	Hammer 403	Lustrous white + black deposits
	Axe 413	Lustrous white + black deposits
	700 110	
2000 N	<i>Ionitoring</i>	
S1	Bar 10	200mm from socket end on wood side, centre
		blade. Lustrous black
S2	Bar 10	30 mm from socket end, under the wood.
S3	Bar 10	180mm from bar tip on reverse. Pale blue-green
S4	Bar 10	175mm from socket on wood side. Black & loose
S5	Bar 10	500mm from socket end on wood side.
		Turquoise + orange + traces of black
S17	Bar 10	Another sample to replace (and substitute for) S2 which did not give good result
S6	Axe 11	Black powder + blue powder at 47mm from
		cutting edge on side of blade
S7	Axe 11	Black. Close to and probably the same as a large
		corroded and blistered area.
00		73mm from cutting edge and near S6
58	Axe11	Reverse side of blade, 82mm from cutting edge. Part of a black blister (but blister is part hollow).
S9	Axe 11	Underside, 50mm from cutting edge. A black
		blister, taken whole. The cleaved-off blister was
010	Aug 44	Very close to metal.
510		Blue, from eye on underside, poll side.
518	Axe II	Another sample to replace (and substitute for)
		STO which did not give a good result
2001 E	Excavation	
S11	Axe 131	Black powder + traces of blue.
		75mm from cutting edge on one face
S12	Axe 131	Black powder. 110mm from cutting edge on
		same face as S11
S13	Axe 131	Surface corrosion layer, orange, + ?plant
		material. Directly over powder and loose black.
S14	Axe 131	Black powder below S13
S15	Axe 131	Blue powder very near to socket on same edge as S13/S14.

# Appendix 2. Concordance for the XRD results from the archaeological artefacts

Object	Sample	XRD Plot nos	Angle °2θ
1091 Execution			
	MOQ	Notroporded	7 100
	1VI90 M07	Not recorded	7 - 100
Rou 207	IVI97 ME1	Not recorded	7 - 100
Dod 212 P		Not recorded	7 - 100
R00 312 B			7 - 100
Axe 331	<u>P8</u> P4 – P7, P9	Not recorded	7 – 100
Hammer 332	M96	Not recorded	7 – 100
Axe 383	M53	Not recorded	7 – 100
Hammer 403	M52	Not recorded	7 – 100
Axe 413	M55	Not recorded	7 – 100
2000 Monitoring			
Bar 10 (S.1)	U.137	405, 385, 386	15–65
	U.145	410, 413	20–70
Bar 10 (S. 2)	U.143	408	20–70
(S.17)	U.148	414	15–65
Bar 10 (S. 3)	U.144	409, 418	20–70
Bar 10 (S. 4)	U.138	379, 405, 421	15–65
Bar 10 (S. 5)	U.139	407	20–70
Combined spectra for Bar	10	890	25–65
		893	15–65
Axe 11 (S. 6)	U.125	367, 396	15–65
Axe 11 (S. 7)	U.126	368, 397	15–65
Axe 11 (S. 8)	U.124	393, 394	15–65
Axe 11 (S. 9)	U.127	369, 399	15–65
Axe 11 (S. 10)	U.136	378, 417	15–65
(S.18)	U.149	395, 415	15–65
Combined spectra for Axe	11	891	15–65
2001 Excavation			
Axe 131 (S.11)	U.129	371.400	15–65
Axe 131 (S. 12)	U.130	372, 401	15–65
Axe 131 (S. 13)	U.131	373, 391, 402	15–65
Axe 131 (S. 14)	U.132	374, 403	15–65
Axe 131 (S. 15)	U.133	375, 404	15–65
	U.135	377	15–65
Combined spectra for Axe	131	892	15–65
Combined spectra for bar and axe 131	10, axe 11,	894, <u>895</u>	20–65

Appendix 3. XRD spectra for the archaeological iron artefacts excavated in 1981

![](_page_25_Figure_1.jpeg)

a) All artefacts sampled

b) Axe-head 331 detail

![](_page_25_Figure_4.jpeg)

Appendix 4. XRD spectra for the archaeological iron artefacts recovered in 2000–1

#### Bar 10, Axe 11, Axe 131 Fiskerton 7-Sep-2005 10:11 3600 [counts] 2500 1600 900 400 100 0 30 40 50 [°20] 60 U124.RD U125.RD U129.RD U131.RD U144.RD U145.RD

a) Currency bar 10, axe-head 11 and axe-head 131

Selected XRD spectra for archaeological iron artefacts recovered in 2000-1. Lowest spectrum upwards: U124 = axe-head 11 (S.8), U125 = axe-head 11 (S.6), U129 = axe-head 131 (S.11), U131 = axe-head 131 (S.13), U144 = currency bar 10 (S.3), U145 = currency bar 10 (S.1)

Appendix 4. XRD spectra for the archaeological iron artefacts recovered in 2000–1

![](_page_27_Figure_1.jpeg)

#### b) Fiskerton 2000: currency bar 10 (samples 1, 3, 4, 5 & 17)

Lowest spectrum upwards: U145 = S.1 U148 = S.17 U144 = S.3 U138 = S.4U139 = S.5

Appendix 4. XRD spectra for the archaeological iron artefacts recovered in 2000–1

#### c) Fiskerton 2000: shaft-hole axe-head 11 (samples 6–9 & 18)

![](_page_28_Figure_2.jpeg)

Lowest spectrum upwards: U125 = S.6 U126 = S.7 U124 = S.8 U127 = S.9U149 = S.18

Appendix 4. XRD spectra for the archaeological iron artefacts recovered in 2000–1

#### d) Fiskerton 2001: socketed axe-head 131 (samples 11–15)

![](_page_29_Figure_2.jpeg)

Lowest spectrum upwards: U129 = S.11 U130 = S.12 U131 = S.13 U132 = S.14U135 = S.15

# Appendix 5. Visual appearances of the recovered experimental iron bars

Burial period	Rod	Bar	Description	
6 months Rod 1				
6	1	1	Slimy and dark; some orange over the black deposits	
6	1	2	Orange and black slimy deposits	
6	1	3	Orange and black slimy deposits	
6	1	4	Brighter orange layer. Peaty soil	
6	1	5	Brighter orange layer. Peaty soil	
6	1	6	Much dryer	
6	1	7	Much dryer	
6	1	8	Barely corroded	
6 month	ns Rod 2	2		
6	2	1	No oxidation	
6	2	2	Orange deposit under one tie. Black deposits elsewhere	
6	2	3	Very little orange deposits but more black	
6	2	4	More orange and black	
6	2	5	Thicker orange and black	
6	2	6	Pronounced orange staining	
6	2	7	Thick orange	
6	2	8	Dryer. Brighter orange.	
12 mon	ths Roa	11		
12	1	1	Soil with orange corrosion products over black	
12	1	2	Soil with orange corrosion products over black	
12	1	3	Soil with orange corrosion products over black	
12	1	4	Soil with thick orange corrosion products over black	
12	1	5	Soil with thicker orange corrosion products over black	
12	1	6	Soil with orange thick corrosion products over black	
12	1	7	Less corrosion products	
12	1	8	White metal visible plus thin corrosion only	
12 mon	ths Roa	12		
12	2	1	Soil with traces of light brown deposits over black layer adjacent to etched metal	
12	2	2	Similar to (12/2/1) above but more etched, and the	
			surface deposits are orange rather than light brown	
12	2	3	Like (12/2/1) above	
12	2	4	Like (12/2/1) above, plus some patches of bubbly multi-	
			coloured deposits adjacent to metal	
12	2	5	Like (12/2/1) above but with more black deposits	
12	2	6	Like (12/2/1) above but more etched	
12	2	7	As above, much bright orange, over black	
12	2	8	As above, with some shiny black/brown bubbles adjacent to metal	

18 m	onths R	od 1	
18	1	1	Black, silvery, lustrous loose deposits, with bare metal visible below. Sampled the lustrous and black from 4 sides, specifically where it had built up against the Installation Rod.
18	1	2	Bare metal encrusted with black and orange deposits
18	1	3	Lustrous surface with orange deposits
18	1	4	Eroded, with black and orange deposits above
18	1	5	Lustrous, with black and orange deposits above
18	1	6	Lustrous, with black, orange and light brown deposits
18	1	7	Black, orange and light brown deposits
18	1	8	Mare metal at one end, with mainly dark deposits
18 m	onths R	od 2	
18	2	1	Orange corrosion products over thick black deposits
18	2	2	Eroded metal with thin brown-orange deposits
18	2	3	Eroded metal with black-orange deposits
18	2	4	Thick black deposits under orange
18	2	5	Eroded metal plus orange and black deposits
18	2	6	Eroded metal plus orange and black deposits
18	2	7	Slightly eroded metal plus orange and black deposits
18	2	8	Orange over black deposits

# Appendix 6. Concordance for the XRD results for the experimental iron samples

Rod	Bar	Sample XRD Plot Nos		Angle °2θ		
6 month burial duration						
1	1	U 153	432, 433, 447	20 – 70		
1	2 a	U158	437	20 – 70		
1	3 b	U157	436, 450	20 – 70		
	3 c	U169	465	20 – 70		
	3	5071	693, 712, 713	10 – 90		
1	4	U167	460, 461	20 – 70		
1	5	U155	435, 449	20 – 70		
1	6	U170	466, 467	20 – 70		
1	7	5065	668, 676	10 – 90		
1	8	5066	669, 671-675, 681-682	10 – 90		
Comb	ined spectra	plots for 6 month	678	20 – 90		
burial,	, Rod 1 Bars	1 - 8:	677	20 – 70		
			679	20 – 60		
			683	15 – 85		
			680	30 – 50		
2	1	5073	696, 702-706	10 - 90		
2	2	U160	445, 452, 453	20 – 70		
2	3	U168	462, 463	20 – 70		
		5072	694, 695, 714, 715	10 – 90		
2	4	U164	444, 454	20 – 70		
2	5	U165	459, 442	20 – 70		
2	6	U166	458	20 – 70		
2	7	5069	688-691, 710	10 – 90		
2	8	5070	692, 707, 708, 709	10 – 90		
Comb	ined spectra	plots for 6 month	697, 699	10 – 90		
burial,	, Rod 2 Bars	1 - 8:	700	20 – 70		
			701	30 – 50		
12 mo	onth burial d	luration				
1	1	5014	552, <u>553</u>	15 – 70		
		5050	611	10 – 90		
1	2	5023	561, 593, 594, 595	15 –70		
			590, 591, <u>592</u>	10 – 90		
1	3	5018	556,	15 –70		
		5022	560	15 –70		
		5049	606, 607, 608, 609	10 - 90		
1	4	5019 5051	557, 596, 597	15 - 70		
	_	5000	013, 014 550, 500	10 - 90		
1	5	5020	558, 598	15 -/0		
_		5052	615, 616	10 - 90		
1	6	5021	559, 599, 600	15 –70		
		5053	617, 622, 623, 624, 625	10 - 90		
1	7	5024	562, 601, 602, 603	15 –70		
		5054	618, 619, 627, 628, 629	10 – 90		

1	8	5025	563, 604, 605	15 –70
		5055	610, 630, 631, 632, 633	10 – 90
Con	nbined sp	ectra plots for 12	642	15 – 85
mor	nth burial,	Rod 1 Bars 1 - 8:	643	20 – 80
			644	25 – 55
			641	20 – 45
			716	20 - 55
2	1	5056	611, 658, 659	10 – 90
2	2	5057	645, 660	10 – 90
2	3	5058	646, 647, 661	10 – 90
2	4	5060	648, 662	10 – 90
2	5	5061	649, 650	10 – 90
2	6	5062	651, 663	10 – 90
2	7	5063	652, 664, 665	10 – 90
2	8	5064	653, 666, 667	10 - 90
Con	nbined sp	ectra plots for 12	654	10 - 90
mor	nth hurial	Rod 2 Bars $1 - 8^{\circ}$	655	20 - 80
	itir bariai,		656	20 - 65
			657	20 00
-			031	22 00
18 ו	month bu	rial duration		
1	1	5086	758, 795	5 – 100
			823	20 - 90
1	2	5091	764	5 – 100
			849	20 – 90
1	3	5090	763	5 – 100
			848	20 - 90
1	4	5092	765	5 – 100
			847	10 - 90
1	5	5087	759	5 – 100
			846	10 – 80
1	6	5093	766	5 – 100
			845	10 – 90
1	7	5088	760	5 – 100
			844	10 – 90
1	8	5094	767	5 – 100
			843	20 – 85
Con	nbined sp	ectra plots for 18	796	7 – 100
mor	nth burial,	Rod 1 Bars 1 – 8	797	10 – 100
	,		799	20 – 75
			800	20 – 70
			801	20 – 55
			802	20 – 45
			856	10 – 90
			857	20 – 55
2	1	5095	768	7 – 100
			817	15 – 95
2	2	5096	769	7 – 100
			816	10 – 90
			824	10 – 90
2	3	5097	770, 771	7 – 100
			818	10 – 90
			830	10 – 90
2	4	5098	772	7 – 100

			815	10 – 85
			829	10 – 90
2	5	5099	814	7 – 100
			828	5 – 95
2	6	5100	773	7 – 100
			822	20 – 75
			827	15 – 70
2	7	5101	774	7 – 100
			821	15 – 90
			826	20 - 80
2	8	5102	775	7 – 100
			819	10 – 90
			825	20 - 80
Con	nbined sp	ectra plots for 18	803	10 – 100
mor	nth burial,	Rod 2 Bars 1 – 8	804	20 – 75
			805	20 – 70
			806	10 – 55
			807	20 – 45
			854	10 – 90
			855	20 – 55
Wo	ty Drys	torage (Rod Lonly)		
1	1	5074	719	5 - 100
1	3	5075 wet	720	5 - 100
	-	5090 dried	898	20 – 50
			899	20 – 65
1	5	5076	721	5 – 100
1	7	5077 wet	722	5 – 100
		5088 dried	897	15 – 80
Combined spectra for Bars 1, 3, 5 &			808	10 – 80
7: w	7: wet + dry			20 – 75
	-		812	20 – 55
			813	20 – 45

Appendix 7. XRD spectra for the experimental iron samples, 6 months, Rod 1, Bars 1–8

![](_page_35_Figure_1.jpeg)

Upper spectra shown at 20–70° 2 $\theta$ , lower shows detail at 30–50° 2 $\theta$ . Bar 1 is lowest, increasing to Bar 8 at the top (U153 = Bar 1; U158 = Bar 2; U169 = Bar 3; U167 = Bar 4; U155 = Bar 5; U170 = Bar 6; 5065 = Bar 7; 5066 = Bar 8).

Appendix 8. XRD spectra for the experimental iron samples, 12 months, Rod 1, Bars 1–8

![](_page_36_Figure_1.jpeg)

![](_page_36_Figure_2.jpeg)

Upper shows spectra at  $10-90^{\circ} 2\theta$ , lower shows detail at  $25-55^{\circ} 2\theta$ . Bar 1 is lowest, increasing to Bar 8 at the top (5050 = Bar 1; 5048 = Bar 2; 5049 = Bar 3; 5051 = Bar 4; 5052 = Bar 5; 5053 = Bar 6; 5045 = Bar 7; 5055 = Bar 8).

Appendix 9. XRD spectra for the experimental iron samples, 18 months, Rod 1, Bars 1–8

![](_page_37_Figure_1.jpeg)

![](_page_37_Figure_2.jpeg)

Upper shows spectra at  $10-90^{\circ} 2\theta$ , lower shows detail at  $20-55^{\circ} 2\theta$ . Bar 1 is Lowest, increasing to Bar 8 at the top (5086 = Bar 1; 5091 = Bar 2; 5090 = Bar 3; 5092 = Bar 4; 5087 = Bar 5; 5093 = Bar 6; 5088 = Bar 7; 5094 = Bar 8).

Appendix 10. XRD spectra for the experimental iron samples, 6 months, Rod 2, Bars 1–8

![](_page_38_Figure_1.jpeg)

Upper shows spectra at  $20-70^{\circ} 2\theta$ , lower shows detail at  $30-50^{\circ} 2\theta$ . Bar 1 is lowest, increasing to Bar 8 at the top (5073 = Bar 1; U160 = Bar 2; U168 = Bar 3; U164 = Bar 4; U165 = Bar 5; U166 = Bar 6; 5069 = Bar 7; 5070 = Bar 8).

Appendix 11. XRD spectra for the experimental iron samples, 12 months, Rod 2, Bars 1–8

![](_page_39_Figure_1.jpeg)

Upper shows spectra at  $10-90^{\circ} 2\theta$ , lower shows detail at  $20-55^{\circ} 2\theta$ . Bar 1 is lowest, increasing to Bar 8 at the top (5056 = Bar 1; 5057 = Bar 2; 5059 = Bar 3; 5060 = Bar 4; 5061 = Bar 5; 5062 = Bar 6; 5063 = Bar 7; 5064 = Bar 8).

Appendix 12. XRD spectra for the experimental iron samples, 18 months, Rod 2, Bars 1–8

![](_page_40_Figure_1.jpeg)

Upper shows spectra at  $10-90^{\circ} 2\theta$ , lower shows detail at  $20-55^{\circ} 2\theta$ . Bar 1 is lowest, increasing to Bar 8 at the top (5095 = Bar 1; 5096 = Bar 2; 5097 = Bar 3; 5098 = Bar 4; 5099 = Bar 5; 5100 = Bar 6; 5101 = Bar 7; 5102 = Bar 8).

Appendix 13. XRD spectra for the experimental iron samples, comparing wet and dry storage conditions for Bars 1, 3, 5 and 7 from Rod 1, 18 month burial duration

![](_page_41_Figure_1.jpeg)

Upper shows spectra at  $10-80^{\circ} 2\theta$ , lower shows detail at  $20-45^{\circ} 2\theta$ . From lower to top: 5074 = Bar 1 wet stored; 5086 = Bar 1 dried: 5075 = Bar 3 wet stored; 5090 = Bar 3 dried: 5076 = Bar 5 wet stored; 5087 = Bar 5 dried: 5077 = Bar 7 wet stored; 5088 = Bar 7 dried.