The Upper Gothens buckle: a technical report

1.0 Introduction

A small buckle from Upper Gothens was presented to us for examination and analysis. It had already undergone conservation treatment (Clydesdale, this report). The analysis aimed to verify the conservator's observation that "the X-ray (radiograph)…suggests that the buckle was originally coated with a more radio-opaque metal most likely tin".

2.0 Methodology

A sample of c. 0.3cm was removed from the buckle by cutting with a diamond saw, revealing a cross section of completely mineralised material. Despite the visible lack of evidence for any metal remaining it was decided to proceed with a polished surface, by mounting the sample on metallographic resin and grinding and polishing with 6, 3 and 1 micron diamond paste. The polished block was subsequently carbon coated in preparation for SEM-EDAX analysis.

3.0 Results

Figure 1a shows a SEM-BS (scanning electron microscope backscattered) image of the section. Two areas retaining a metallic component were immediately obvious, amidst a matrix of mineralised material. SEM-EDAX spot analyses were undertaken at various locations within the matrix and the metallic component.

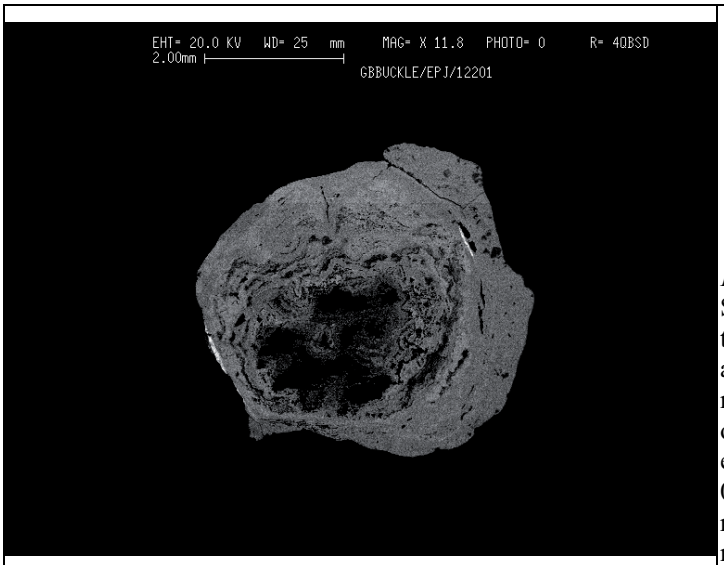


Figure 1a:
SEM-BS image of the section of the UG buckle – cut across the artifact and showing extensive mineralisation with the exception of two metallic areas a) on the edge (bottom left) and b) about 0.5mm to the interior (upper right). The core is completely mineralised. (bar=2 mm; x11.8)

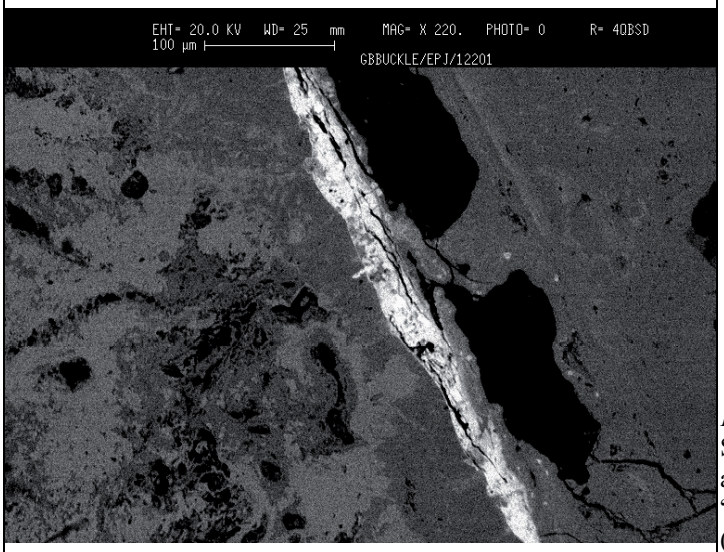


Figure 1b:
SEM-BS image of the metallic area to the right, about 0.5mm "inland" from the outer surface (bar=100microns; x220).

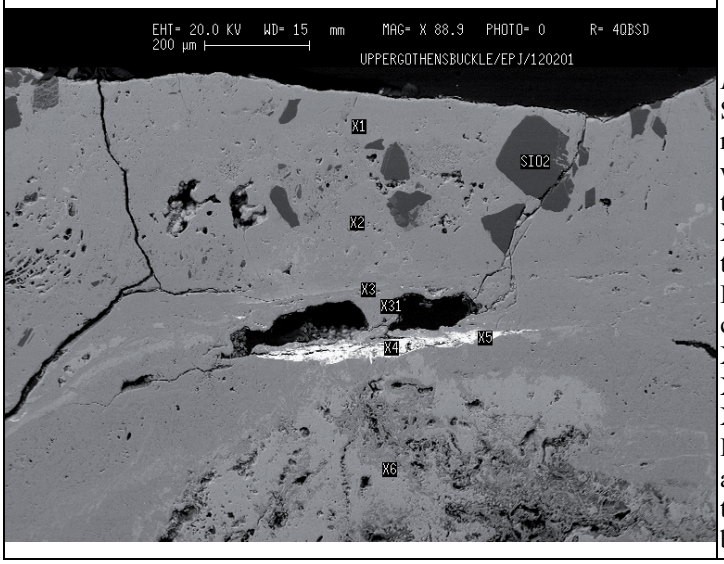


Figure 1c:
SEM-BS image of the same remnant of metallic constituent within the mineralised body of the buckle. Spots X1, X2, X3, X31, X4 and X5 correspond to the points where spot SEM-EDAX analyses have been carried out (see also range of XRF spectra). X1=iron, X2=iron, X3=iron, X31=iron and tin, X4=iron, copper and tin, X5=tin Large angular (black) inclusions are grains of quartz adhered onto the surface, in the course of burial (bar=200microns; x88.9).

Qualitative XRF spectra are shown in Figures 2 and 3. Figure 2 shows a general analysis of the first metallic remnant (shown in the bottom left of Figure 1a). It consists of tin, with small amounts of iron and copper, either as a single metallic phase or as a number of intermetallic components. It is therefore clear that tinning did take place. Figure 3 shows the results of the qualitative analyses carried out on a number of spots, from the surface of the sample to the metallic remnant (top right of Figure 1a). The exact location of these spots can be seen at higher magnification in Figure 1c. X1, X2 and X3 showed only iron; X4 showed tin with small amounts of iron and sulphur, while X31 showed iron as a major component with small amounts of tin. The results of the above analyses suggest that the iron oxide layer overlaying the metallic tin-rich strip must be due to volume expansion due to weathering. The structure and composition of the second metallic strip (bottom left of Figure 1a) can be seen in greater detail in Figures 1e and 1f.

Table 1 shows the results of quantitative spot analyses at different areas within the strip. Angular grains of a copper-tin intermetallic compound with small amounts of lead are obvious. The thin band is another iron-tin intermetallic as are other areas either iron-tin rich (spots X1) or tin-iron rich (spots X2). The real question is the extent to which there is evidence for an interface between the tin-rich layer and the iron substrate. Line scans with the CAMECA electron microprobe (Figure 4) show that the drop in tin is abrupt and over a distance of c. 1 micron. There is no gradual loss of tin away from the tin-rich fusion zone. So it is quite clear that "tinning" consists of the formation of an iron-tin intermetallic compound rather than of pure tin. The quantity of tin ranges from a high of 92% to a low of 6% implying that "tinning" was not even. The presence of lead in small quantities suggests recycled pewter as the raw material.

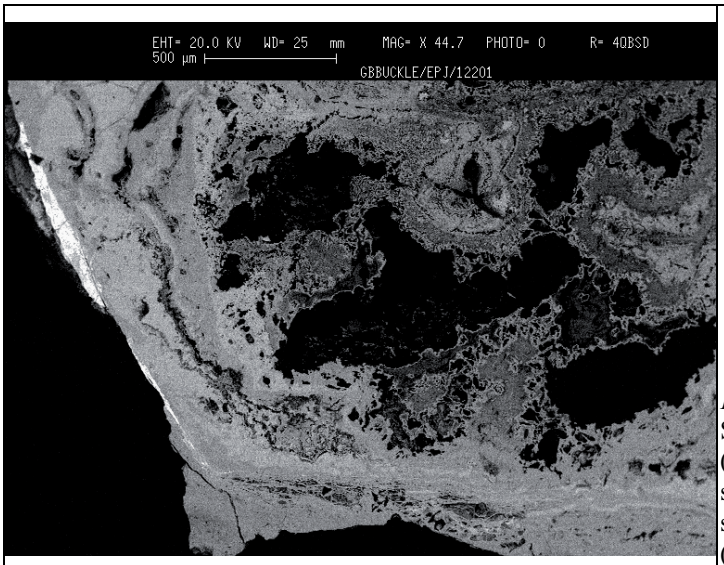


Figure 1d:
SEM-BS image of the UG buckle (bottom left section of Figure 1a) showing metallic remnants on the surface of the sample (bar=500microns; x44.7).

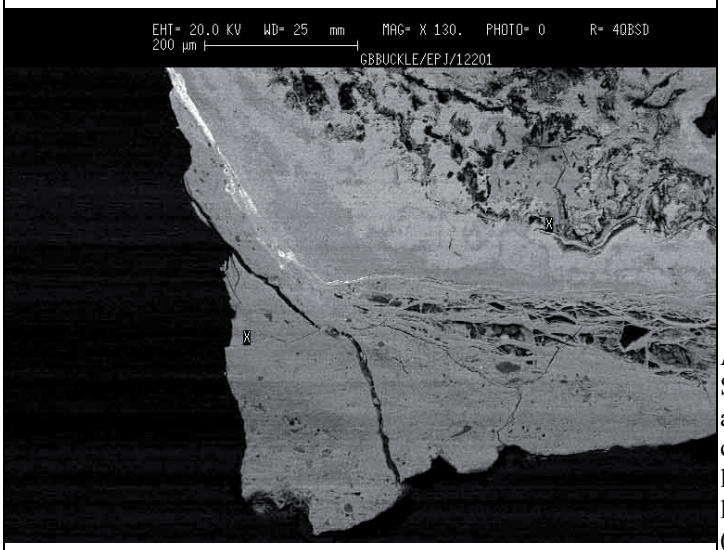


Figure 1e:
SEM-BS image of section above at higher magnification with corrosion induced – filament – like structure. The bright hair-like strands are a tin-rich area (bar=200microns; x130).

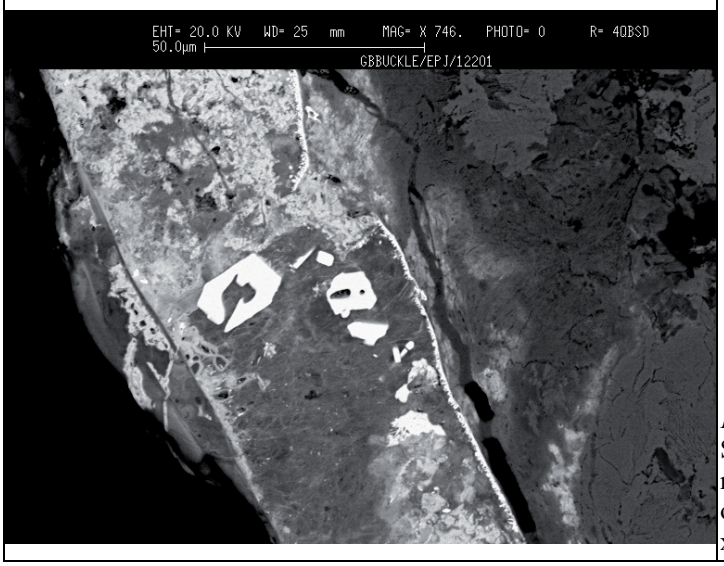


Figure 1f:
SEM-BS image of remnants of metallic areas with angular grains of copper - tin(bar=50microns; x746).

4.0 Discussion

Tinning of copper and bronzes for the purpose of producing a shiny surface (simulating silver) has been practiced since "ancient times". Apparently EBA flat bronze axes from Scotland have been found to have a thin coating of tin (Coles 1971) The most common application would be on mirrors to produce the necessary reflecting surface (Meeks 1986). But tinning was also practiced on iron surfaces. Jope (1956) has demonstrated on the basis of a collection of artefacts from Oxford that tinning of iron spurs was widespread among lorimers, the practice continuing over a long period from the 10th to the 17th century. The technique used is called fusion-plating. In this process tin (or bronze) filings are sprinkled on a clean iron surface and then heated. The clean surface was maintained by using an organic "resin" or whale-oil (Singer et al 1956, p689-690) to avoid oxidation of the iron surface. The "antiquity" of the practice can be traced back certainly to the 11th century as described by Theophilus in his treatise *On Divers Arts*.

"If you want to coat an iron object with tin, first file it and, before touching it with your hand, while it is freshly filed, throw it into a pot of melted tin with tallow and stir it about with tongs until it becomes white. Then take it out, shake it vigorously, and clean it with bran and with a linen cloth. When you have made iron locks and hinges for small chests and for doors, finally heat them and smear them with pitch! The nails, however, should be tinned" (Hawthorn and Stanley-Smith, 1963, p187)

Tin-lead alloys appear also to have been used. A lead-tin alloy, a soft solder consists of 63% tin and 37% lead and fuses at c. 183C. Tin-plating of thin sheets of wrought iron metal is the precursor of the tin canning

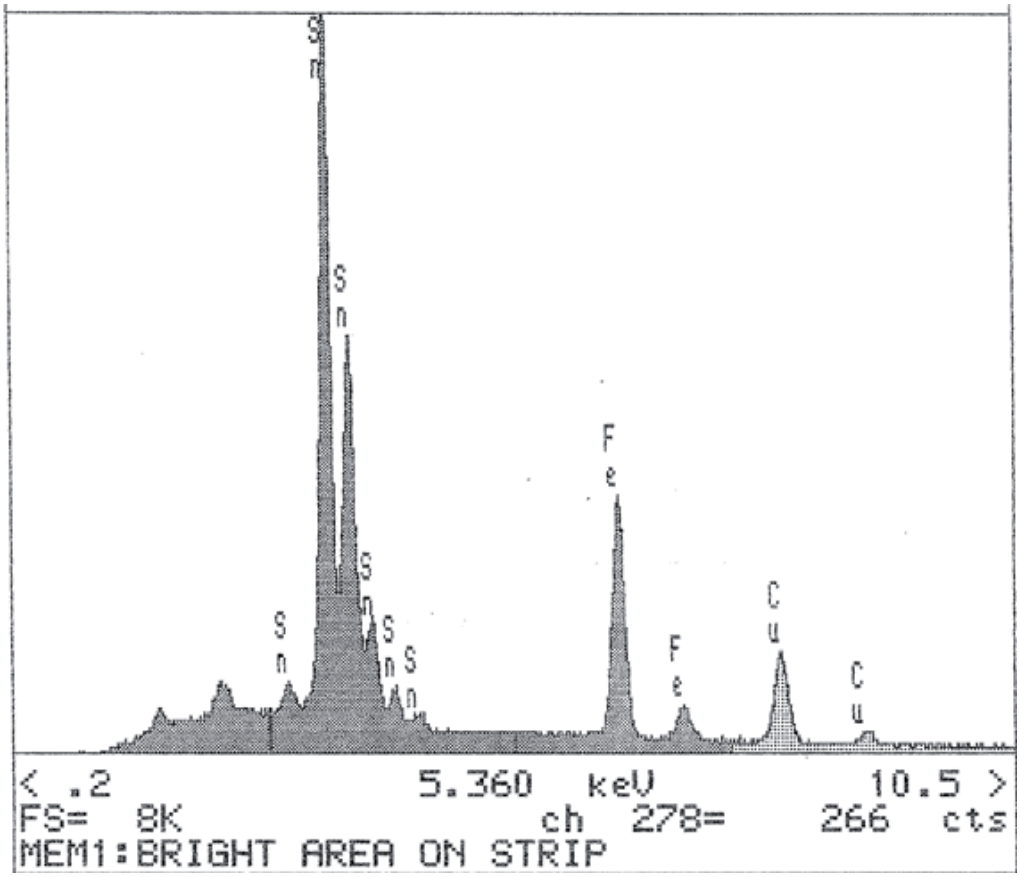


Figure 2: Qualitative analysis of one of the two tin-rich strip at area of the sample showing tin as the major constituent with iron and copper as the minor ones.

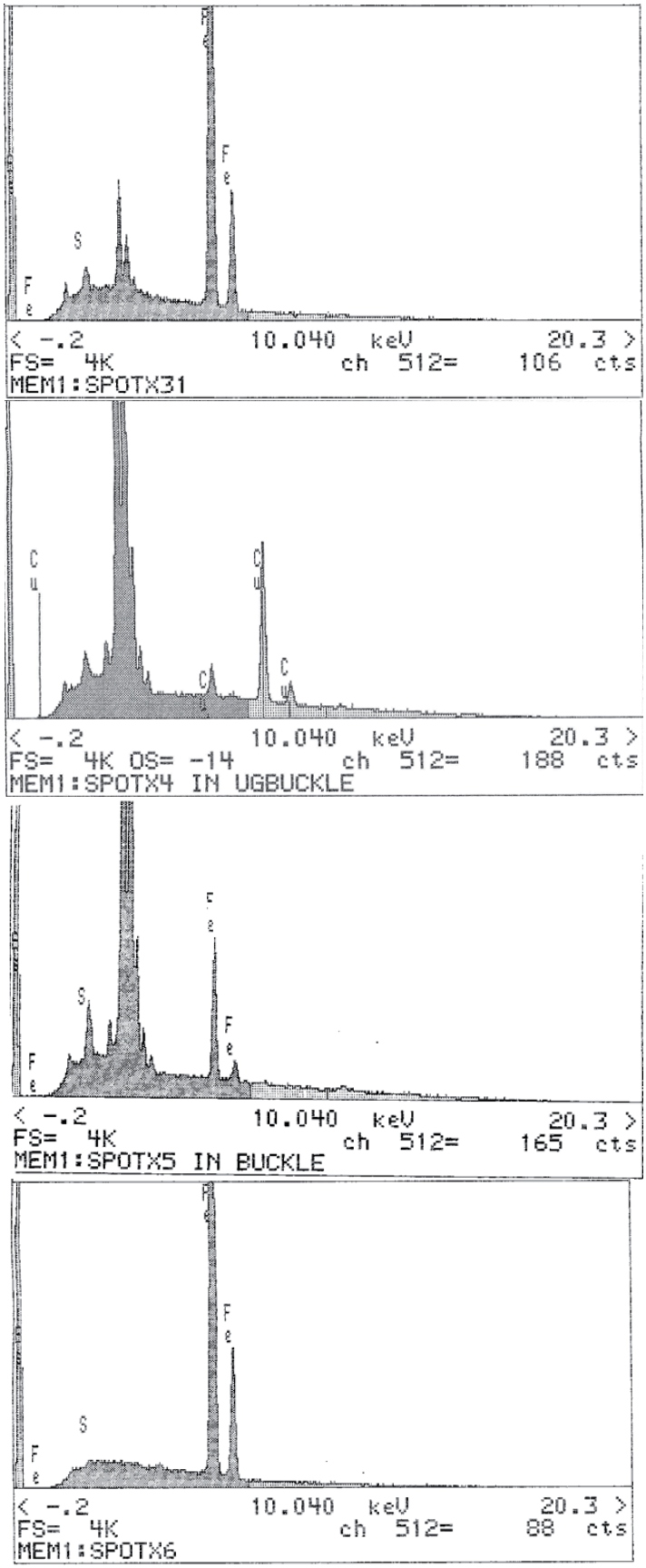
industry for food preservation set in place by the early 19th century. Electroplating of tin on steel followed soon after (Meeks 1986).

The tinning of medieval ironwork appears to have been primarily a spurs makers practice at least as testified from the examination of such artefacts dating from the 10th to the 17th century (Jope 1956). It has rarely been detected on other iron objects. It has therefore been suggested that the production of spurs was a specialist area, while other specialist groups made other parts of the harness accompaniments, for example the stirrups. By the 13th century there was a separate Spurriers' Guild in London and their records would suggest that the spurs were their only product. The spurs demonstrate a high fashion product made for the middle and upper "echelons" of society, which was established in later Saxon England and continued through to at least the 17th century (Jope 1956, p36).

The UG tin buckle may have been part of a spurrier's accroutement as seen in Figures 5a, 5b and 5c reproduced from Jope (1956, fig 14). Recycled pewter appears to have been used for this particular artefact. Tin metal for that pewter may have been derived form bronze remelting. On application, a tin iron fusion layer develops giving the buckle its silvery shine. Its present thickness does not exceed 200 microns but the original width of the iron-tin layer may have been larger.The presence of remnants of a thin tin-iron layer c. 0.05mm "below" the surface can be attributed to expansion of iron oxides due to weathering.

Given existing archaeological evidence (slag sample), it is not possible to tell whether this buckle was produced locally in the smiddy within the boundaries of the UG palisade. Yet one could envisage a spurrier working away quietly on his merchandise, whichever that one might be.

Figure 3: Qualitative analyses of the tin-rich areas of the second strip.



5.0 References

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Hawthorn J.G. and Stanley Smith C., 1963, *Theophilus on Divers Arts: The foremost Medieval Treatise on Painting, Glassmaking and Metalwork*, Dover Publications Ltd p187)

Jope E. M., 1956, The tinning of iron spurs: a continuous practice from the tenth to the seventeenth century, *Oxoniensia,* Vol 21, p35-42.

Meeks, N.D., 1986, Tin-rich surfaces on bronze – some experimental and archaeological considerations, *Archaeometry,* Vol 28(2), p133-162.

Singer et al, 1957, *The History of Technology c.1500- c.1750*, Vol III, Clarendon Press, Oxford.

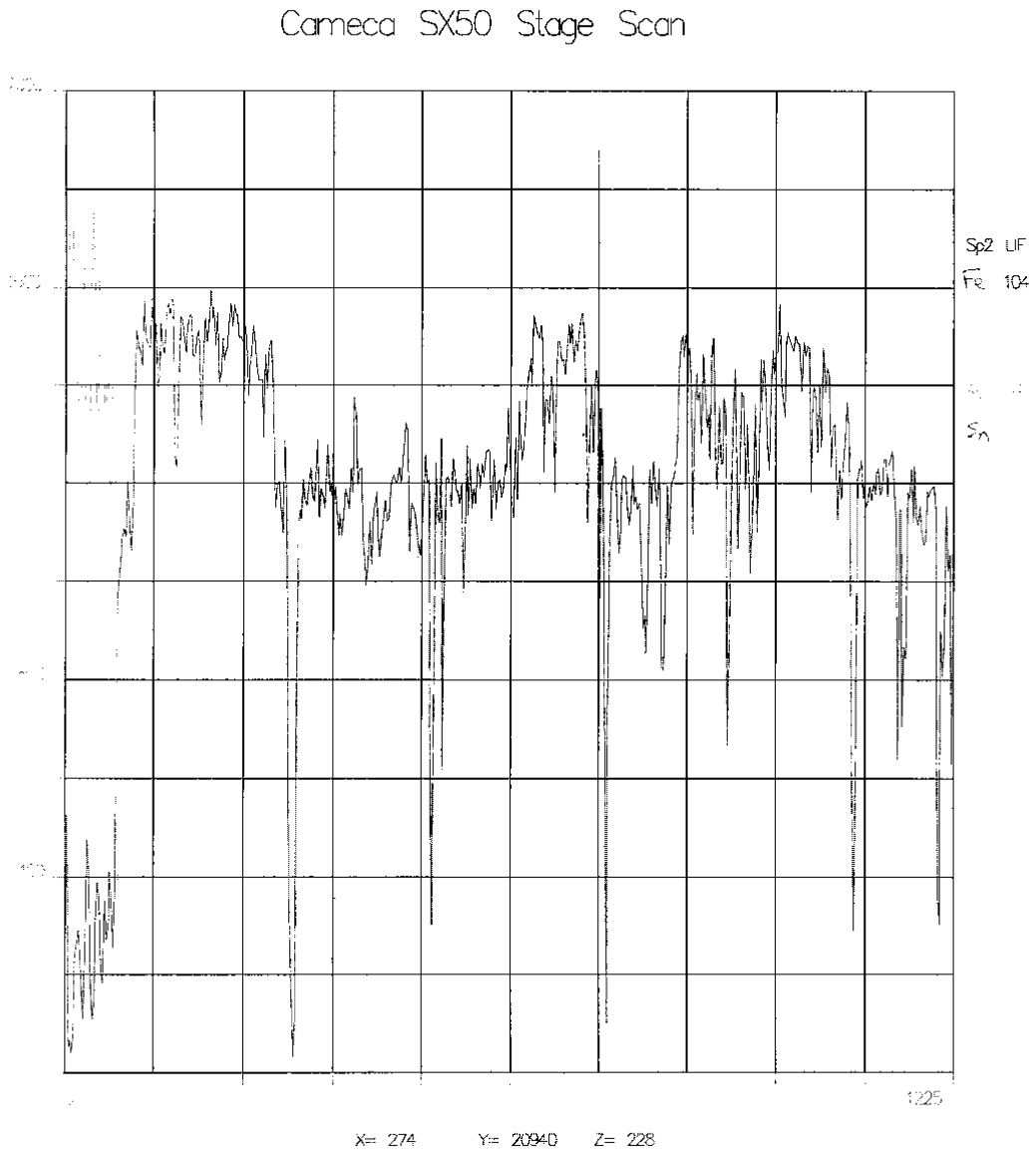

Figure 4: Line scans for tin and iron taken with a Cameca Electron Microprobe over area A shown in Figure 1d.

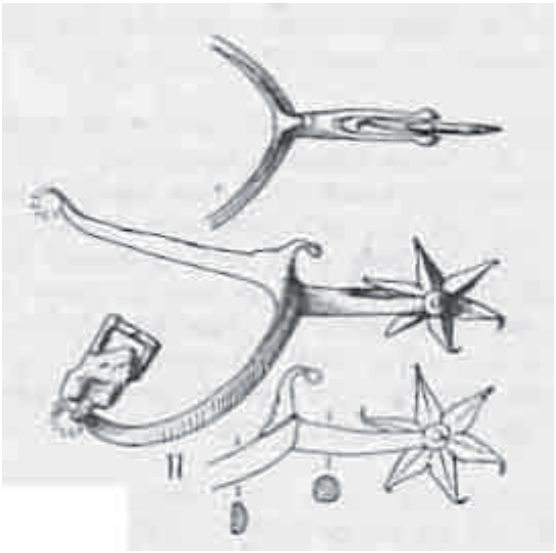

Figure 5a:
Rowel-spur of tinned iron found at Ixworth, Suffolk (adapted from Jope 1956, fig14)

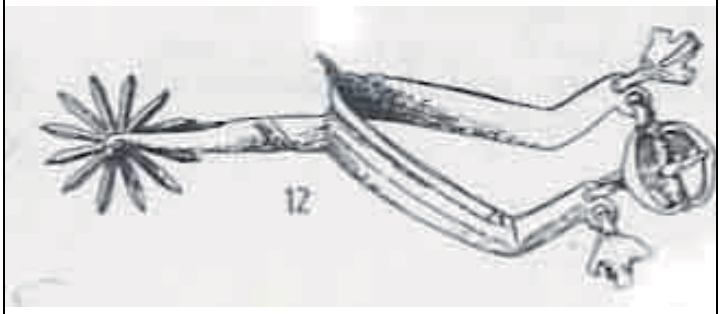

Figure 5b:
Rowel-spur of tinned iron found at Oxford (adapted from Jope 1956, fig14).

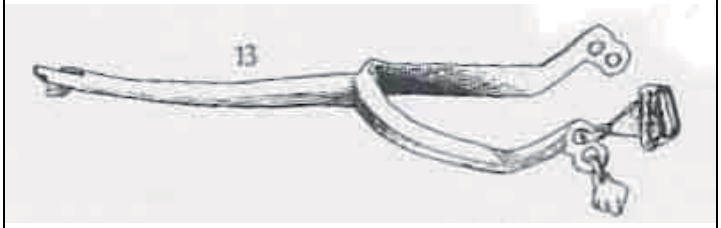

Figure 5c:
Rowel-spur of tinned iron found at Oxford (adapted from Jope 1956, fig14).