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Analysis of technical ceramics, Wormington – Sapperton Pipeline

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Abstract

Assessment of archaeometallurgical residues from Plot 20.02 revealed several fragments of clay wrap or shroud, that may have originated during one of several metallurgical techniques, including brazing, carburising, carburising and protection from either caburising or decarburising.

To investigate these materials, qualitative analyses were made by portable X-Ray fluorescence spectrometry. Analyses were taken from a variety of spots on the ceramic wraps, as well as from a number of sherds of moulds from Plot 07.09.

The pattern of elemental analyses of these various materials showed low levels of contamination by copper, lead and zinc in the moulds, but no such contamination was recognisable in the analyses of the wrap fragments. It is argued that this, together with the very high levels of iron incorporation into the slagged areas of the wraps, suggests that wraps were probably employed for carbon control or hardening purposes. The morphology of two of the wrap fragments would be compatible with clay applied to the back of a blade – this suggesting they were used to prevent carbon-uptake during caburisation of the edge. The third piece is more complex and the nature of the original artefact is unknown, although the wrap may have been used for a similar purpose.

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Methods

The programme of analysis was focused on three fragments of partially vitrified technical ceramic from Plot 20.02 (together with an isolated bleb of partially melted ceramic) and two fragments of ceramic mould from Plot 07.09. During the assessment of the archaeometallurgical residues (Young 2011), it was suggested that the ceramics from Plot 20.02 may have been employed to coat an iron object during the process of brazing. Examination by handheld XRF was therefore recommended in order to test for contamination of the coating by the brazing metal. Similarly testing of the mould fragments was undertaken to examine whether they could provide evidence for the nature of the cast metal.

The specimens were analysed on a purely qualitative basis using a Bruker Tracer III-SD portable X-Ray fluorescence spectrometer. The instrument was operated with the Bruker 'yellow' filter (300µm Al + 25µm Ti), at 40kV and 9.60 µA, with a filament current of 189 µA, for 100s.

The instrument was controlled by a PC running Bruker's S1PXRF with spectra stored as pdz files and csv files. The images presented in Figure 1 are produced from the csv output.

Peak heights have been calculated for the Fe Kα, Cu Kα, Zn Kα, Pb Lα1 and Zr Kα peaks in Excel. The Sn peaks are too small for reliable measurement.

This project was undertaken for Ed McSloy of Cotswold Archaeology.

Background

In one form of brazing (the joining of iron by the use of a filler metal, usually of copper alloy, with a high melting temperature), a clay wrap or shroud encloses the piece(s) of iron to be brazed, along with the copper alloy brazing metal. The package is heated to above the melting point of the brazing metal, which then tracks across the surface of the iron and is drawn into any small gaps on metal joins (see the illustrations provided by Young 2012 for the use of such wraps or shrouds). Such brazing processes are well-documented for weights (Söderberg & Holmquist Olausson1997), iron handbells and animal bells (Young 2012) and padlocks (Gustafsson 2005; Söderburg 2008) amongst other artefact types. Although these examples are dominantly early medieval in age, some artefacts present in the British Iron Age are also suggestive of having been produced by brazing. Theophilus described this approach to brazing in the early 12th century (Hawthorne & Smith 1979, 186).

Other purposes for coating iron in clay wraps also exist and are primarily associated with carbon control and case hardening. These uses for a clay wrap involve either a protective role, in which the clay acts as a barrier between the iron and the hearth environment (variously to inhibit either carburisation or decarburisation), employed a clay slurry as medium to bind a carbon source to the surface of iron to be carburised or as a wrap to contain the reducing environment produced by an organic medium such as leather wrapped around the object to be hardened (Söderberg 2008). Such case hardening techniques were described by Theophilus in the context of the manufacture of files (Hawthorne & Smith 1979, 94–5).

In all of these uses, wraps can typically be distinguished from moulds by possessing a low-density, often partially bloated, fabric, with at least localised external vitrification. They are typically pale grey in colour, sometimes with a paler surface (although this may also be either dark and slagged or coated in a transparent green wood ash glaze). Wraps may preserve impressions on their inner surfaces of either the iron object itself or of material bound onto the surface of the iron (such as cloth, leather or brazing metal).

Results

The wraps (Plot 20.02)

The examined materials comprised a ceramic wrap fragment and a bleb of apparently associated partially melted ceramic from context 527 (labelled as 'Coat A' and 'bleb' in the analytical tables and diagrams), together with two fragments of wrap from content 538 (labelled 'coat B' and 'coat C' in the analytical tables and diagrams).

The nine spectra taken from various points on these specimens are all broadly similar in most respects, but differ markedly in the size of the iron peaks (Figure 1).

The pXRF spectra from the 'bleb' and from the dark, slagged external surface of 'coat B' showed very iron-rich compositions (with peak heights of 250,000 to 270,000 counts).

Lower, but still very strong, iron peaks (50,000 to 135,000 counts) were present in the spectra for points on the unvitrified external surface of 'coat A', the unvitrified interiors of both 'coat B' and 'coat C', as well as a vitrified area on the outside of 'coat C'.

Lower iron peaks (<50,000 counts) were present in spectra from the unaltered external surface of both 'coat B' and 'coat C', as well as from a small slag drip attached to an otherwise unaltered surface on 'coat A'.

Thus, the iron enrichment in the ceramic was observed locally both on internal and external surfaces of the wraps. The unaltered areas of clay showed spectra broadly similar to those of analyses taken of the mould fragments (see below).

Further details of the chemical trends with the analyses are illustrated by the plots of raw peak heights of the Fe Kα, Cu Kα, Zn Kα, Pb Lα1 and Zr Kα peaks shown in Figures 2 and 3.

In Figure 2, the peak height for zirconium (a trace element within the ceramic) declines as it becomes diluted by iron during the slag-forming process. The data shown for the wraps in Figure 3 show a similar inverse relationship between the peak heights for iron on one hand and copper, zinc, and lead on the other. This is compatible with the similar simple dilution of a ceramic component containing trace levels of these last three elements, by the addition of iron. The correlation line between copper and iron shows the least decline with rising iron, which gives room for a small element of doubt about simple dilution for this element.

Nonetheless, the data provide little or no support for a significant level of copper alloys entering the slagged material during the process. It therefore appears unlikely that these residues are from brazing. The degree of contamination of the ceramic by iron at high temperature is significant, and indicates that the wraps were employed in a process involving iron, even if that process is unlikely to have been brazing.

The moulds (Plot 07.09)

Two fragments of moulds were examined, both from context 115 (one was labelled as mould, the other as a tuyère). Each item was analysed on both surfaces.

The pXRF spectra are broadly similar to those from the iron-poor parts of the wraps described above (Figure 1). However, in detail (Figures 2 and 3), it can be seen that although the zirconium peaks are very similar in height to analyses from the wraps with the same iron peak height, the peak heights for copper, zinc and lead are all relatively elevated (the peak heights for copper, zinc and lead are all still low in absolute terms). Moreover, it is noticeable that the peak heights for those elements are fractionally higher for spectra taken from the internal surfaces than the external.

This pattern suggests that some contamination of the ceramic by copper alloy has taken place. The particular levels of contamination by the different alloy metals is not interpretable in terms of an alloy composition, not only because of the qualitative nature of the XRF data, but also by the differing patterns of reaction of these elements with ceramics (Kearns *et al*. 2010). In particular, the observable contamination by zinc does not indicate that the copper alloy was a brass; this element often accumulates in the body of

the ceramics and only a very low level need have been present in the original metal. Although the peaks were too low for useful measurement, they were present and the data are compatible with a tin bronze being the metal employed in the casting, as might be expected for the earlier Iron Age (Dungworth 1997).

Interpretation

The moulds (Plot 07.09)

The analyses of the moulds provide evidence for very slight contamination of the clay by the elements of the copper alloy. Such contamination is at very low levels, since little metal is transferred into the ceramic during the process. Indeed, it is conceivable that some of the contamination might be due to preparation of the moulds in an already contaminated workshop area.

The key benefit of the analyses is really as a control to the analyses of the wraps from Plot 20.02. They demonstrate that low levels of contamination may be detected by the methodology of the project and thereby assist in determining the significance of the results from the wraps.

The wraps (Plot 20.02)

The analytical data suggest (but do not prove) that brazing was not the purpose of the clay wraps.

The three fragments of wrap present two different morphologies:

Two pieces, 'coat A' from (527) and 'coat C' from (538), have a morphology with a flat inner face with one lower side upturned at right angles. 'Coat b' is up to 27mm wide, with an upturned edge of approximately 3mm. The surface is more strongly slagged than for 'Coat C'. In 'coat C' the two sides are 12mm and 21mm wide, with a length of 55mm; at one end the wrap thins to a thin slagged margin, suggesting the metal may have protruded beyond the wrap. For both examples the wrap is crudely formed and has developed deep external fissures on firing, with local external vitrification and bloating.

These two pieces would be compatible with a clay coating applied to the back of a knife or other blade, when the smith was attempting to carburise the edge only. The inner contact surfaces are smooth and suggest direct contact with the iron, rather than the use of the ceramic to hold a case hardening material in place. However, the use of these pieces to carburise, with the section extending beyond the clay remaining decarburised (in the manner of the manufacture of files as described by Theophilus and discussed by Söderberg, 2008; see above) cannot be entirely excluded.

The third piece, 'coat B' from (538), has a more complex morphology, showing closely adjacent fragments of sub-circular section and curved form, one of which extends to the slagged margin of the ceramic. The two curved imprint sections are of approximately 10mm diameter and are almost, but not precisely, aligned in a single plane. The loner piece has a radius of curvature suggestive of an overall external diameter of approximately 80mm, with the smaller piece suggestive of a diameter of approximately half of that. The longer length of curved impression extends to the surface of the clay, at which point the clay is strongly slagged.

This piece had the morphology most suggestive of brazing, being strongly suggestive of the use of brazing to join two 'rings'. However, the analyses of this piece are comparable to those of the two pieces described above, sharing the same lack of evidence for influence from a brazing metal. The pXRF spectra for the iron-poor areas of this piece do show higher peaks for zinc than do most of the other spectra from the wraps, but they are still lower than the corresponding peaks from the outside of the mould fragments.

If this piece is correctly interpreted as not from brazing and a similar protective role is suggested for the wrap as for the two other pieces, then an interpretation of the artefact represented is problematic. The curved sections visible on the interior of the wrap are not easily identifiable, but would appear to be decorative. Decorative ironwork would not normally require the heat treatment or hardening processes implied by the wrap. If the two curved pieces were not to be joined by the process involving the wrap, then the possibility exists that they are parts of the same piece, perhaps with a scroll-like form. Curved terminations to hardened (or steeled) items are also hard to match in the archaeological record, but some fire-strikers have curved terminations. One piece shears may have an annular spring that would need protection from the steeling process employed on the blade, but typically early shears have a curved flat spring, not a round-sectioned spring.

Summary

The analyses suggest that clay wraps were from a process of ironworking, probably to protect part of an artefact from carburisation while another section was being steeled and not from brazing. The alternative, that the clay wraps held a case-hardening medium in place during heating, appears less likely, but is also possible.

Insufficient remains of wraps survive to determine precisely what artefacts were being made. In the case of the smaller pieces ('coat A' and 'coat C') protection of the back of a blade appears likely. For the more complex item, 'Coat B' the artefact remains unknown.

The moulds show analyses compatible with being used to cast a tin bronze. Their main value is in demonstrating that the trace levels of coper alloy contamination that might be expected to have ensued form using clay wraps in brazing should have been detectable by the techniques employed here.

Figure Captions

Figure 1

Upper: pXRF traces for analyses taken on mould fragments from Plot 07.09.

Lower: pXRF traces for analyses taken on wrap fragments from Plot 20.02.

Figure 2

Binary plot showing the relationship between the peak height of zirconium with that of iron.

Figure 2

Binary plots showing the relationship between peak heights of copper, zinc and lead with those of iron.

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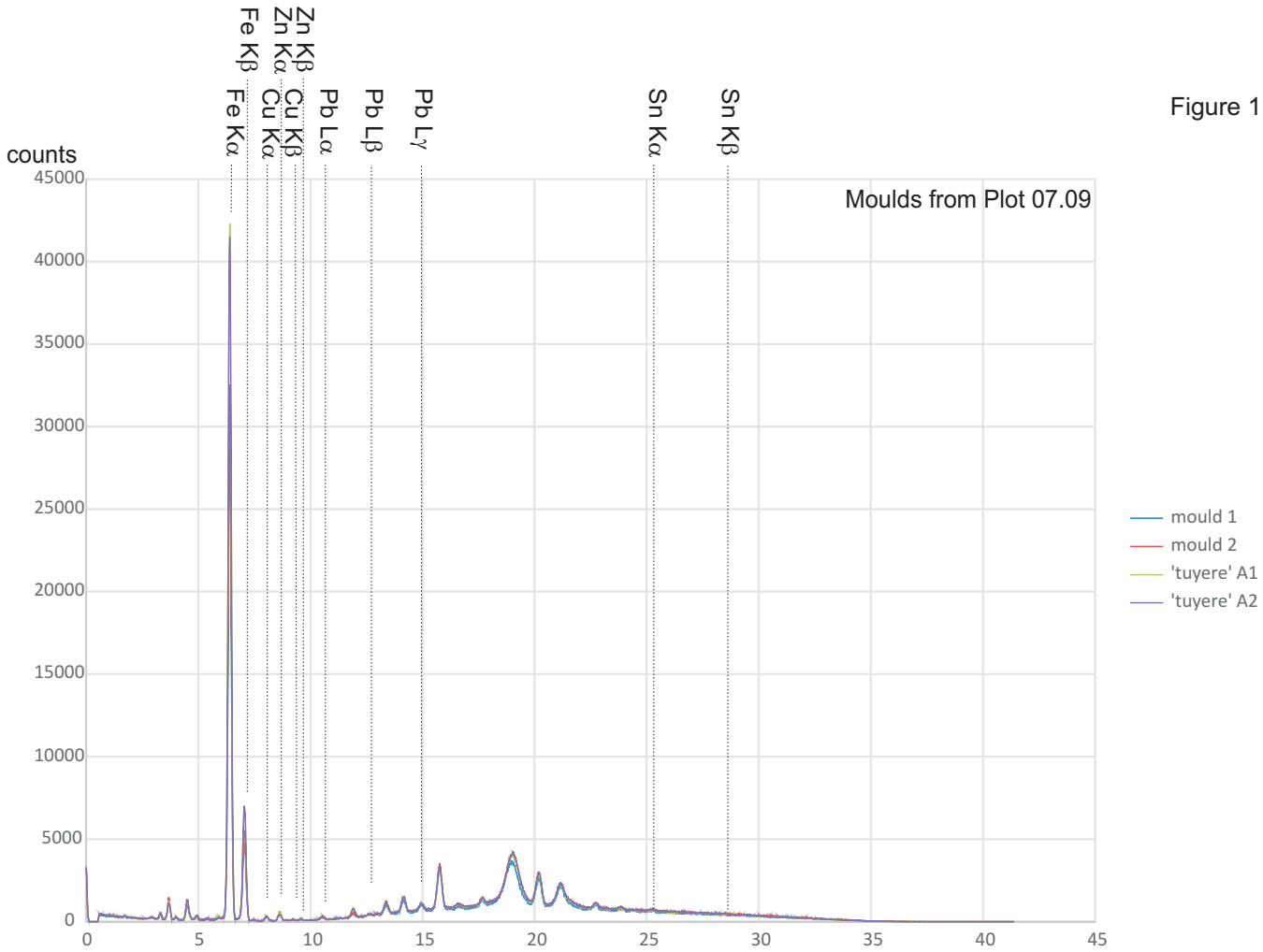
Figure 1


Fe Kβ
Fe Kα
Zn Kβ
Zn Kα
Cu Kβ
Cu Kα
Pb Lα
Pb Lβ
Pb Lγ
Sn Kα
Sn Kβ
counts
Moulds from Plot 07.09
mould 1
mould 2
'tuyere' A1
'tuyere' A2

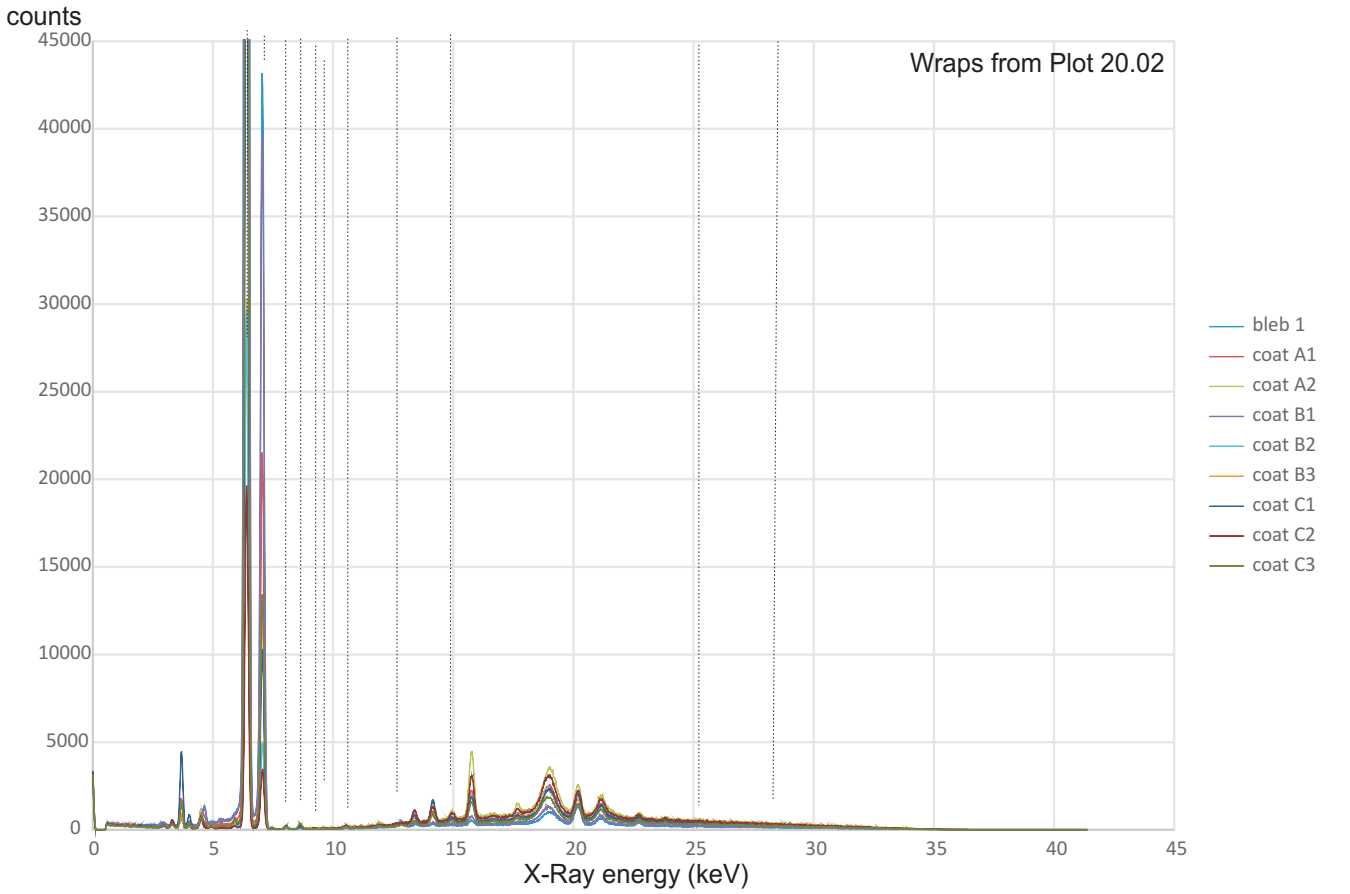

counts
Wraps from Plot 20.02
bleb 1
coat A1
coat A2
coat B1
coat B2
coat B3
coat C1
coat C2
coat C3
X-Ray energy (keV)

Figure 2

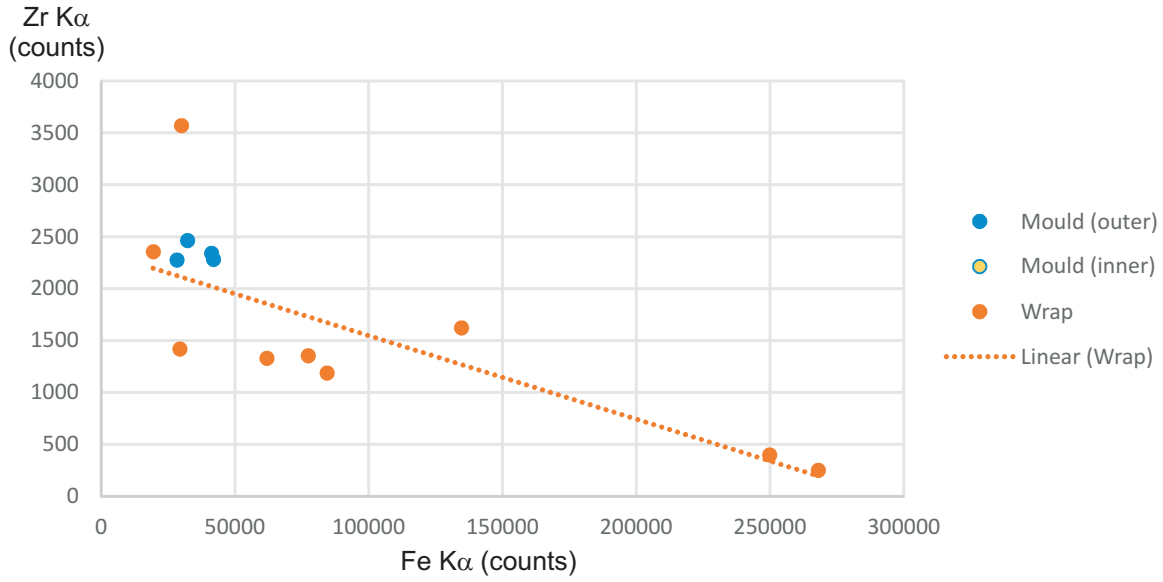
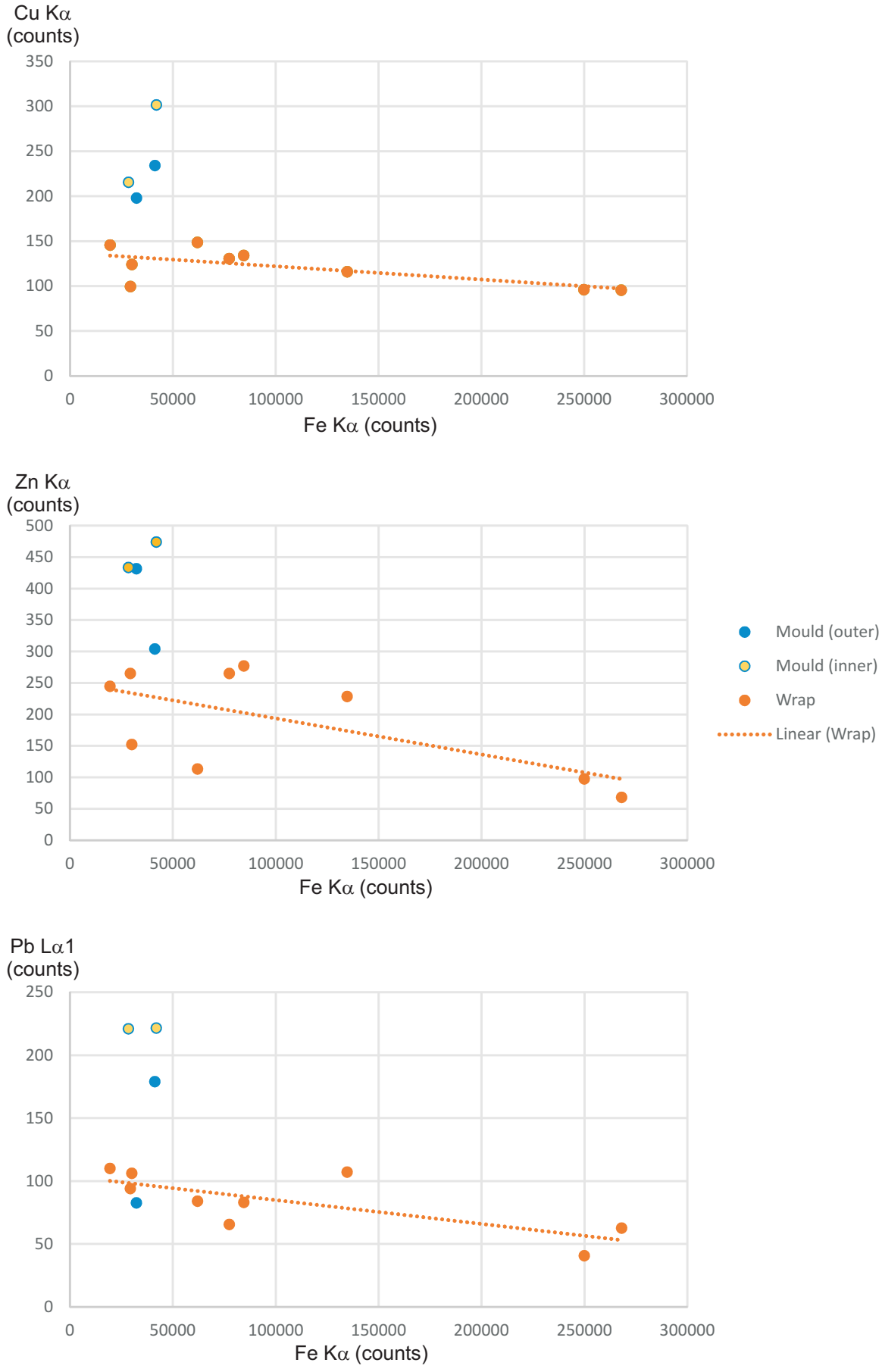

Zr Kα (counts)
4000
3500
3000
2500
2000
1500
1000
500
0
0
50000
100000
150000
200000
250000
300000
Fe Kα (counts)
Mould (outer)
Mould (inner)
Wrap
Linear (Wrap)

Figure 3


Cu Kα (counts)
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300
250
200
150
100
50
0
0
50000
100000
150000
200000
250000
300000
Fe Kα (counts)
Zn Kα (counts)
500
450
400
350
300
250
200
150
100
50
0
Fe Kα (counts)
Mould (outer)
Mould (inner)
Wrap
Linear (Wrap)
Pb Lα1 (counts)
250
200
150
100
50
0
Fe Kα (counts)

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