WINCHESTER
A CITY IN THE MAKING

Archaeological excavations between 2002 – 2007
on the sites of Northgate House, Staple Gardens and the former Winchester Library, Jewry St

Section 4.2

Surface X-ray fluorescence (XRF) analysis of non-ferrous metalworking debris

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Surface X-ray fluorescence (XRF) analysis was used to determine the metals present within visible metallic droplets on the surfaces of 17 crucibles, and hence suggest which types of alloy were being melted and cast at site. Four other samples were also analysed (Table 1). Metals from the melting process will also be present within vitrified areas, where they have combined with other elements from the hearth and from the crucible fabric itself, but the relationship between the elements found in vitrified layers and those of the original metal load is even more complex than that between the metallic deposits and the metal load. Therefore analysis was carried out on those samples where metallic deposits could be clearly seen.

OCCasionally vitrification with copper alloy deposits becomes detached from the crucible, and one sample (NH4491) is probably an example of this. Another fragment seems be from a large, thick-walled crucible (NH4694); although there are no metallic droplets, the inner surface was analysed. Two other samples were analysed, one (NH4623) has a crucible form, but with oxidised surfaces and the other (NH3571) is a piece of shaped, fired clay, also oxidised, with possible metallurgical connections. Lastly, although there is only a small amount of copper alloy waste at the site, one large irregular mass (SF 541, CC1519) was selected for analysis.

Using surface XRF on untreated samples such as these, it is not appropriate to calculate exact percentages of each element present in the droplets, due to the complex effects of heating and corrosion on element proportions. However, the relative size of the peaks can be related to the amount of the elements present, to some degree, given in Table 1 as ‘trace’, ‘present’ and ‘present in abundance’.

The equipment used was an Oxford ED200 air path system with a rhodium X-ray tube, operating at 46kV and 200μA, at the National Museum of Scotland laboratories. The sample spot size was 1.5x3mm and the counting time was 100 seconds.

Results

All the analyses on metallic droplets showed that copper alloys were being melted and cast at the site. Copper, zinc and lead were detected in each case, and tin was also detected in the majority of cases. Iron was also detected in each analysis because iron is present in most early copper alloys, as well as in the crucible fabric and because it is easily detectable by surface XRF. Other relevant elements (*eg* nickel, arsenic, antimony, silver) were sought but not detected.

Table 1: XRF analyses of crucibles and other metalworking debris*

context	SF	phase	building	Sample ID	XRF
CC1519	541	6	BE 2	CA waste	**Cu Sn** Pb Zn
CC3151	338	6	BE5	crucible	Cu Zn Pb
NH1022		5	SE2	crucible	Cu Zn Pb Sn
NH2240		5	BW4	crucible	**Zn** Cu Pb (Sn)
NH2356		5	BW4	crucible	Cu Zn Pb
NH2444		2.4		crucible	Cu Zn Pb
NH2459		5	BW4	crucible	Cu Pb Sn(Zn)
NH2577		5	BW4	crucible	**Zn** Cu Pb
NH2583		5	BW4	crucible	**Zn** Cu Pb
NH3528		5	BW4	crucible	Cu Pb Sn (Zn)
NH3558		5	BW4	crucible and ?crucible	Cu Pb (Zn)
NH3571		5	BW3	ceramic	only Fe
NH3669		4.2	BW3	crucible	Cu Zn Pb (Sn)
NH4085		4.2	BW2	crucible	Cu Pb Sn (Zn)
NH4394		4.2	BW2	crucible	Cu Pb Sn (Zn)
NH4394	266	4.2	BW2	crucible	**Zn** Cu Pb Sn
NH4401		4.2	BW2	crucible	Cu Zn Pb Sn
NH4464	279	4.1	BW2	crucible and vitrification	**Zn Pb** Sn Cu
NH4491	281	4.1	BW2	vitrification	Cu Zn Pb Sn
NH4535		4.1	BW2	crucible	**Zn** Cu Pb Sn
NH4623		4.1		crucible?	only Fe
NH4694	-	2.4		crucible	Pb, Zn (Cu)

Only non-ferrous metals are noted, except where iron alone was detected.* ***Bold* *type is used where the metal is particularly abundant and brackets where there is only a trace.*

Many of the copper alloys can be characterised as either zinc-rich or tin-rich. Five samples (NH 2356, 2444, 2577, 2583 and CC 3151) are amongst those with the highest levels of detectable zinc, and revealed no tin at all. Two samples (NH 2240, 3669) had significant amounts of zinc and only very low levels of tin. These seven samples can be characterised as being brass-like. Conversely, four samples showed only very small traces of zinc (NH 2459, 3528, 4085, 4394) but plenty of tin, more characteristic of bronzes. Seven analyses (NH 1022, 4394, 4401, 4464, 4491, 4535 and CC1519) showed all four major elements clearly present, although zinc was more prominent than tin in three of these (NH 4394, 4464 and 4535). These probably reflect quaternary copper alloy, where zinc, tin and lead were all important alloying elements; this includes NH4491, the sample of copper-alloy debris within vitrification and CC1519, the copper alloy waste. One sample (NH 3558) showed copper, lead and only a tiny trace of zinc, so is only classifiable as a copper alloy.

Amongst the other samples selected for analysis, only iron was detected on both NH4623 (a crucible form, but with oxidised surfaces) and NH3571 (shaped, fired clay, oxidised). There is therefore no clear analytical evidence that these were used for metalworking although, according to specialist opinion (see Cotter *Digital Section 1.3*), the 'unused crucible' samples are unlikely to have been designed as lamps. NH3571 may be considered with the other fired clay material at the site (see Poole *Digital Section 5*). Analysis confirmed that the large possible crucible (NH4694 – Phase 2.4) was probably in contact with a copper alloy at high temperatures, since large zinc and lead peaks and a small copper peak were observed.

Discussion

The analysed crucibles come from Phases 2.4 to 6, with a concentration in Phases 4.1, 4.2 and 5. They come from five properties BW2, BW3, BW4, SE2 and BE5, with seven examples from BW2 and seven from BW4. It is difficult to see any clear patterns within these phases and properties, but notably five of the six quaternary alloys are from BW2, and four of the brass alloys from BW4. However, the four brass alloys from property BW4 were all found on fragments (NH2240, 2356, 2583, 2577) with walls that were

distinctly thinner than those of the average crucibles, about 4.9 mm, compared with averages between 6 and 7mm. This suggests that these four samples originated from a single crucible, broken and scattered over several contexts within the same property. The wall thicknesses of the other analysed crucibles are more typical of those found across the site, so the same situation may not have applied elsewhere. This example serves to warn against over-interpretation of numbers of crucibles present, and hence the intensity of production.

The wide range of copper alloys used in the late Saxon period included zinc-rich and tin-rich alloys (brasses and bronzes, respectively), with various amounts of lead. There is evidence for increasing use of brass in this period, compared to the early and middle Saxon periods (*eg* Blades 1995). The small number of qualitative analyses is not sufficient to give a true assessment, particularly if some of the samples may be duplicates.

At other sites, certain crucible forms are used preferentially for melting particular metals. For example, at Coppergate, York, Stamford Ware was often used for melting silver (Bayley 1992, fig 328). Two main fabric groupings are seen within crucibles at the current site, sandy wares with or without organic tempering. However, there is not sufficient overlap between the crucibles with XRF analyses and those which have had fabric analysis, so it is not possible to determine whether particular copper alloys were associated with the sandy ware with organic tempering.

Examples from other contemporary Winchester sites were also used for copper alloy working (Bayley and Barclay 1990, 175-197), including crucibles from Assize Courts, Lower Brook St, Cathedral Green and Wolvesey Palace. XRF analyses on metallic deposits also showed the presence of lead in most cases, with traces of zinc and/or tin, indicating the same range of copper alloy types as at the current site. However, the other Winchester sites also provided substantial evidence for precious metalworking, mostly in the form of silver traces on crucibles, with a significant number of heating trays and parting vessels, which show silver and gold were being refined. This is admittedly from within a larger sample size (about 400 sherds of crucibles and related material from all the sites). Crucibles used for melting silver were also a dominant feature at amongst around a thousand samples at Coppergate, York, and a smaller number used for melting

gold and copper alloys (Bayley 1992). On the basis of plentiful scrap, Bayley (*op cit*, 823) identified the copper-alloy industry at Coppergate as being primarily wrought, rather than cast. There is no evidence for such an industry at the present site.

Soil analysis (MacPhail and Crowther 2008, 5-6) showed industrial-related dumped soils in property BW5 had elevated levels of the heavy metals Pb, Zn and Cu, but these were not at levels that would have been 'sufficient in themselves to provide unequivocal evidence of non-ferrous metalworking.' Only a small amount of copper alloy waste was found, including a little spillage, and some traces of copper alloy within non-diagnostic ironworking slags (Starley 2008). It should be noted that the small size of crucibles would have meant only small amounts of metal would be melted, hence only minor quantities of metal were available to be lost or discarded during working. Furthermore, it seems likely that small artefacts would be cast at a workbench rather than on the workshop floor (as for late medieval cauldrons), which would allow a 'cleaner' operation with less metal loss. Of the small amount of mould evidence at the site (see Poole *Digital Section 5*), an example of a mould for a decorative fitting (CC2237 – Property BE4 –Phase 5) would fit with this type of working.

The site provides only limited evidence for copper alloy casting, probably of small decorative objects, and no evidence of precious metalworking.

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