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Seventeenth Century Copper Alloy Working from Head Street, Colchester, Essex

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Summary

Excavation at Head Street, Colchester revealed a number of 17th century pits cutting underlying Roam layers. At least one pit produced large quantities of ceramic mould; some of which appears to have been for the manufacture of bells while some appears to have been for the manufacture of cauldrons. Seven fragments of copper alloy and copper alloy slag were examined using a scanning electron microscope and energy dispersive spectrometer. The compositions and microstructures of the samples indicate the casting of a copper alloy rich in antimony. This alloy was not used for the manufacture of bells but was used for casting everyday objects, such as cauldrons. The ore(s) used to produce this alloy can be found in Britain and elsewhere, however, given the date, a source in Germany is most likely.

Keywords

Metalworking non-Fe

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Introduction

The site at Head Street, Colchester (TL 9936 2508), excavated by Colchester Archaeological Trust in 2000, produced evidence for Roman occupation which was disturbed by Post-Medieval pits and foundations. One of these pits (F106) contained waste from 17th century copper alloy casting, including ~300kg of mould debris, slag and amorphous lumps of copper alloy. Some mould fragments included the impression of the letter M (used by the Gray family of bell casters who were active in the 1630s). Some of the mould fragments appeared to be for the manufacture of bells while others appeared to be for the manufacture of vessels. Samples of slag and metal were submitted for analysis to investigate the nature of the copper alloys being cast. Bells were usually cast from high tin bronzes (Tylecote 1986: table 23) while vessels were usually cast from mixed alloys, often with high levels of antimony and arsenic (Werner 1976).

Selection and Preparation of Samples

Seven samples from Pit F106 were selected for examination (Table 1) from each of the three principal layers (L21, L22 and L30) and from a large (~300mm high) lump of slag (from L22). The excavator (Brooks *personal communication*) suggested that the three layers *may* represent three different casting episodes.

Table 1. List of samples selected for examination and analysis

Sample	Feature	Layer	Bag	Material
1	F106	21	1876	Slag
2	F106	21	1876	Slag with attached ceramic
3	F106	22	1875	Slag
4	F106	22	1875	Metal
5	F106	22	2659	Slag
6	F106	30	1577	Slag
7	F106	30	1577	Metal

The samples were all mounted in cold-setting acrylic resin and polished to a 1-micron finish. The samples were examined with light and electron microscopes, before and after etching with ferric chloride. Chemical analyses were carried out on areas and spots using the energy dispersive detector attached to the scanning electron microscope (SEM-EDS).

Description of samples

Each of the samples is described below and illustrated where appropriate. The chemical analyses are gathered in tables 2 (metal) and 3 (slag and ceramic).

<u>Sample 1</u>

This slag is glassy, porous and contains a high proportion of silica inclusions (probably sand), numerous antimony bronze droplets and occasional copper sulphide inclusions (figure 1). The antimony bronze droplets have a sufficiently high antimony content for a second phase to be present. The analysis of the copper sulphide inclusions (see table 2) shows the sulphide to be Cu_2S (analysed atomic ratio of Cu to S of 2.05).

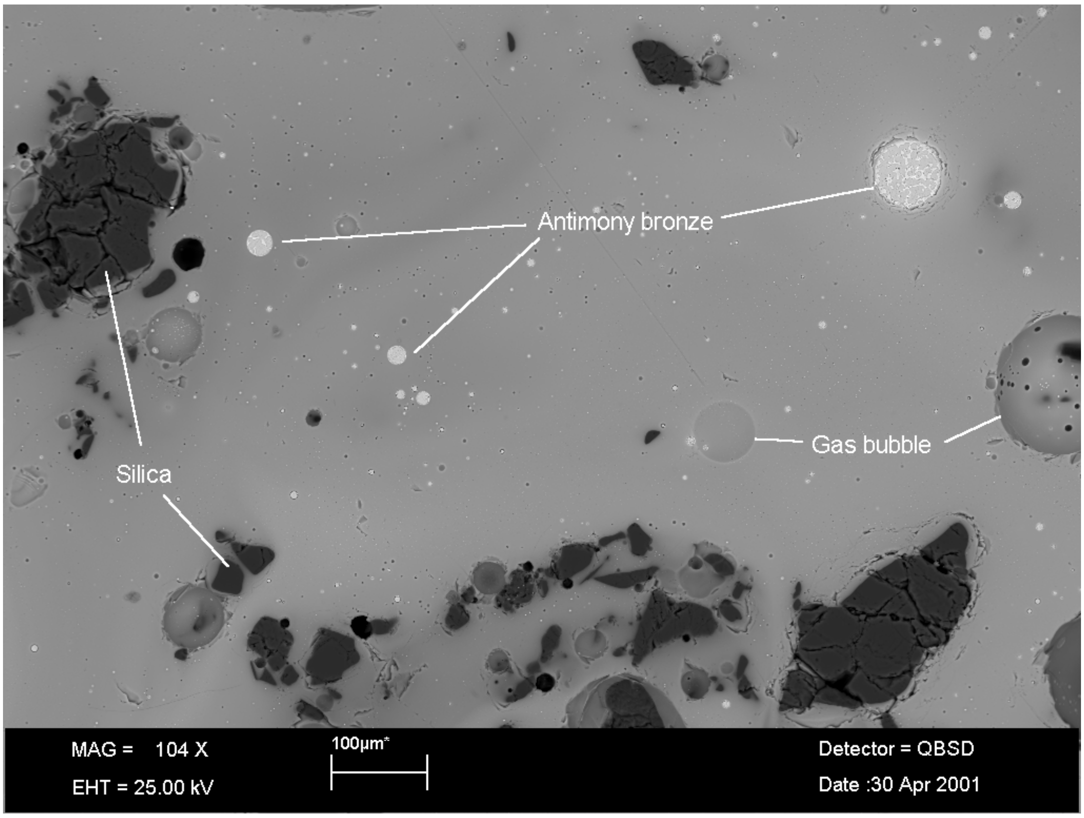

Figure 1. SEM image of sample 1 showing glassy slag with silica inclusions, gas bubbles and antimony bronze droplets

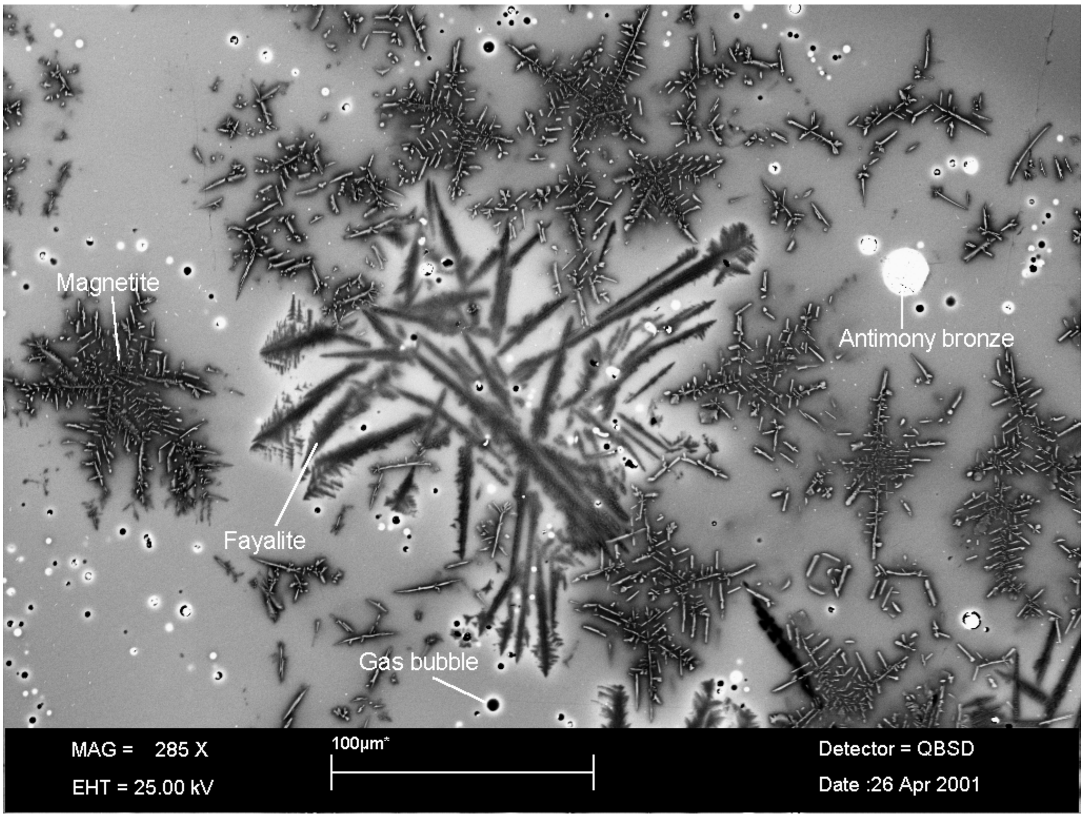

Figure 2. SEM image of sample 2 showing droplets of antimony bronze (bright), dendrites of magnetite (grey) and laths of fayalite (dark grey)

Sample 2
This sample consists of highly vitrified ceramic material with attached slag. The ceramic may be part of the wall of a hearth or furnace, or part of a mould ingate. The slag is glassy but it does contain a number of crystalline phases (laths of fayalite and dendrites of magnetite) as well as lead-rich and antimony bronze droplets (figure 2). The lead-rich droplets also contain antimony and oxygen and approximate to $PbSb_2O_7$. The antimony bronze droplets usually have sufficient antimony for a second phase to be present.

Sample 3
This slag is glassy, porous and contains numerous silica inclusions (probably sand) as well as droplets of copper, copper oxide and antimony bronze (figure 3). Analysis of the copper oxide shows that it is probably Cu_2O (atomic ratio of Cu to O of 1.95). As before, the antimony bronze shows two phases.

Sample 4
This metal is a rather porous antimony bronze, which contains an antimony-rich second phase as well as copper sulphide and lead-rich inclusions. Analysis of the antimony-rich second phase indicates that this is approximately Cu_2Sb (atomic ratio of Cu to Sb of 2.07), i.e. the β phase (Scott 1991: 128).

Sample 5
This slag is glassy and contains numerous silica (probably sand) inclusions as well as droplets of copper, copper oxide and antimony bronze (cf. sample 3).

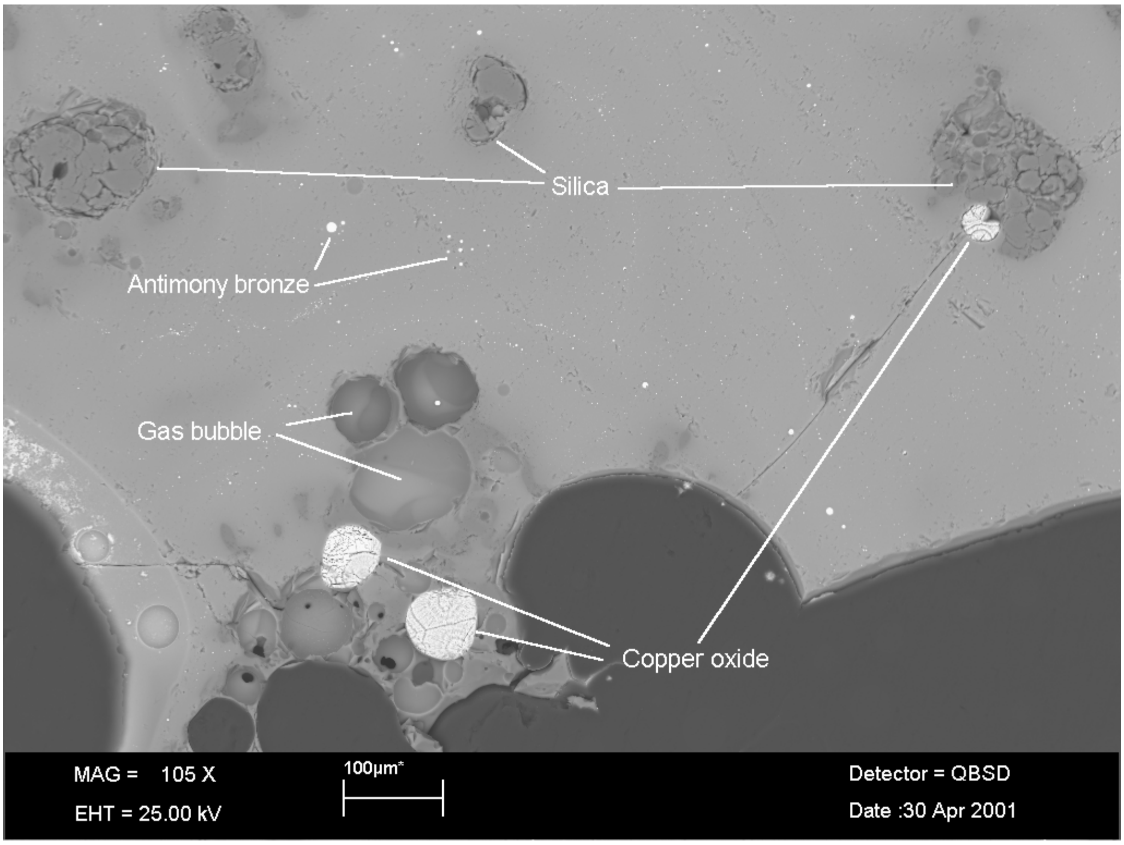

Figure 3. SEM image of sample 3 showing copper oxide and antimony bronze inclusions

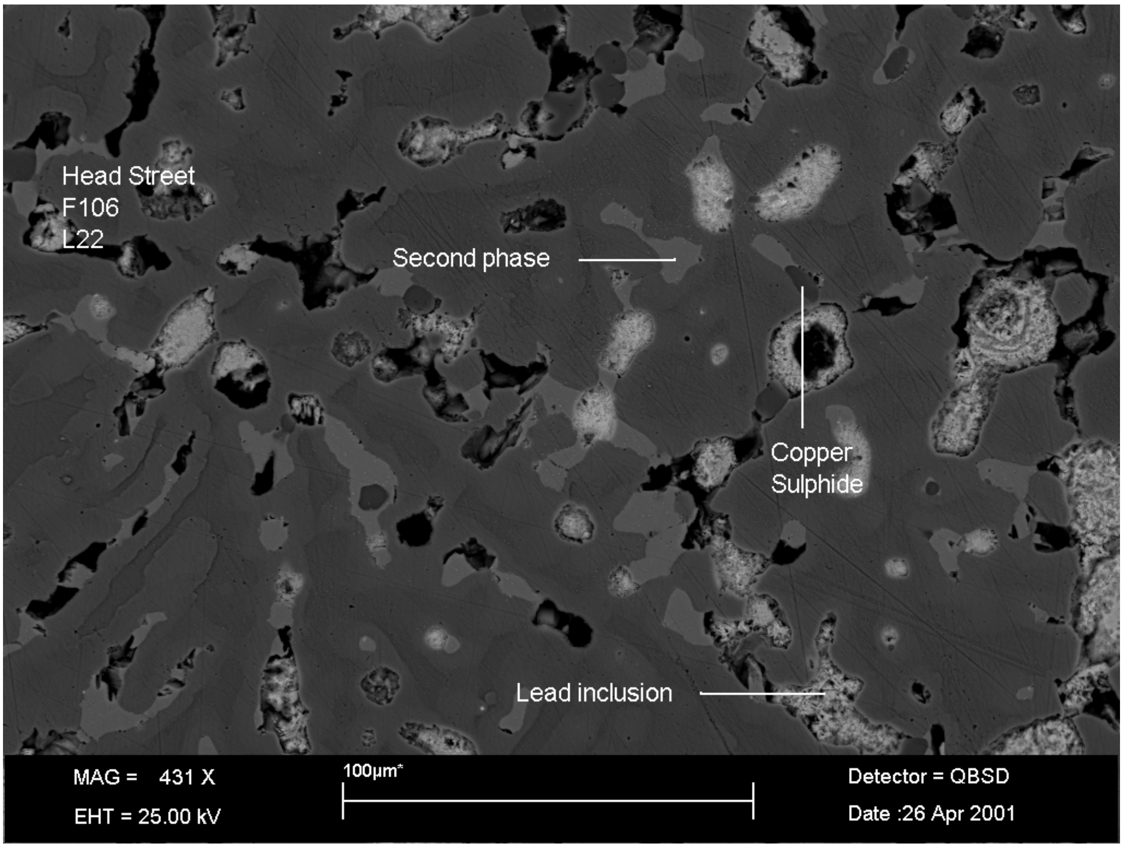

Figure 4. SEM image of sample 4 showing second phase (β), copper sulphide and lead-rich inclusions.

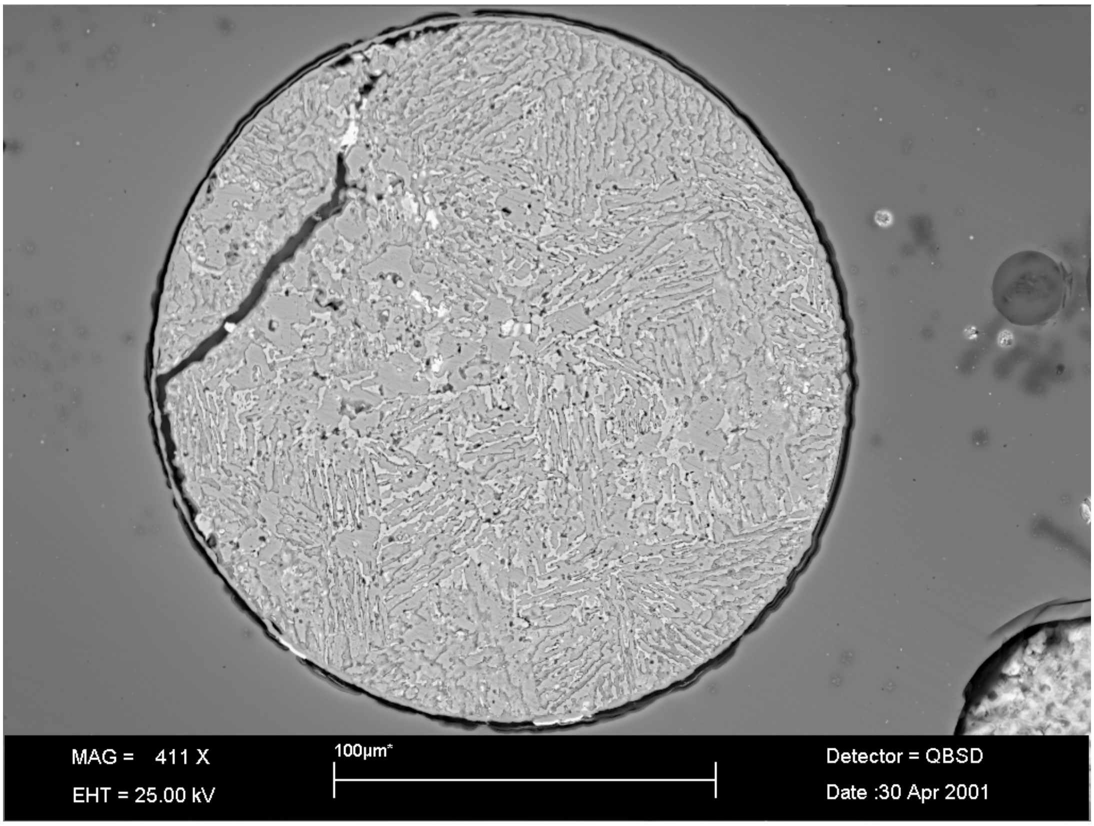

Figure 5. SEM image of antimony bronze droplet in sample 6

Sample 6
This sample consists of a glassy slag with silica inclusions and antimony bronze droplets (figure 5).

Sample 7
This sample consists of an extremely porous antimony bronze which contains an antimony-rich second phase as well as copper oxide, copper sulphide and lead-antimony inclusions (cf. sample 4).

Chemical Analysis

The SEM-EDS analyses were carried out on areas (up to 100 microns across) for the analysis of slag and droplets of metal, or spots (~1 micron in diameter) for the analysis of specific phases (sulphides, etc).

The seven samples examined and analysed fall into two groups: waste metal and slag. The two samples of metal are similar to each other (high antimony bronze containing some lead, tin and arsenic). The five samples of slag are a little more variable but mostly consist of a glassy slag with numerous silica inclusions and antimony bronze droplets. The antimony bronze droplets within the slag have lower lead and sulphur contents than the bulk metal. However, the slag often also contains discrete lead-rich and copper sulphide droplets. In a few cases the lead-rich droplets are actually a mixture of lead and antimony and when present in the slag are occasionally oxidised.

Table 2. Analyses of metal

Sample	Cu	Sb	Sn	Pb	Zn	Fe	Ni	As	S
1 droplet in slag	61.7	23.0	6.6	4.7	nd	0.6	0.6	1.3	nd
1 copper sulphide	77.6	0.6	nd	nd	nd	0.4	nd	nd	20.1
2 droplet in slag	67.3	18.6	7.4	3.9	nd	0.7	0.3	0.7	nd
3 droplet in slag	74.9	18.2	1.6	2.9	nd	nd	0.4	0.9	nd
5 droplet in slag	75.9	20.8	0.8	0.1	nd	0.4	0.3	0.4	nd
6 droplet in slag	65.7	20.5	2.2	2.3	0.6	0.8	0.3	1.6	nd
6 droplet in slag	70.9	7.7	14.1	2.8	0.3	nd	0.3	nd	nd
4 bulk	66.9	10.0	1.2	15.2	nd	0.1	0.1	1.3	0.9
4 antimony-rich phase	51.2	47.3	0.4	nd	nd	nd	0.1	0.1	nd
7 bulk	74.3	10.9	2.0	5.4	nd	0.1	0.1	1.8	0.9

Table 3. Analyses of slag

Sample	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	Fe_2O_3	CuO	ZnO	SnO_2	Sb_2O_3	PbO
1 matrix	0.5	0.9	10.5	45.4	0.9	2.0	1.3	0.7	7.5	0.8	nd	5.6	0.2	23.6
2 ceramic	1.4	1.8	16.3	62.0	1.4	3.2	1.7	1.0	10.0	nd	nd	nd	nd	nd
2 matrix	0.6	0.6	7.8	37.8	0.7	1.5	3.1	0.4	20.6	0.2	0.5	3.6	nd	23.1
3 matrix	0.8	1.0	11.3	65.5	1.0	2.8	3.2	0.7	9.9	1.6	nd	nd	0.4	1.3
5 matrix	0.7	0.8	12.1	58.3	0.7	4.5	2.5	0.8	12.3	0.2	nd	0.7	nd	6.2
5 matrix	0.7	0.8	9.8	46.6	0.7	2.0	3.2	0.6	16.4	0.2	nd	2.4	0.7	16.1
6 matrix	2.5	1.7	7.6	33.8	2.6	1.7	7.7	0.6	12.1	0.2	12.4	2.3	nd	14.1

Discussion

The analysis of the spilt metal and slag associated with bell and vessel mould from F106 shows that alloy being used was an antimony bronze. Analyses of late medieval artefacts has shown that alloys containing appreciable amount of antimony were often used in the manufacture of large vessels (Blades 1995; Werner 1976). Unfortunately much less is known about post-medieval copper alloys. Blades' (1995) study of copper alloys from AD 400 to 1600 includes four 16th century vessels, two of which have appreciable levels of antimony (table 4).

Table 4. Analyses of two 16th century vessels (source = Blades 1995)

Ref	Site	Object	Cu	Sb	Sn	Pb	Zn	Fe	Ni	As	S
535	Deansway	Vessel rim	62.6	3.9	6.0	17.8	0.1	0.1	0.1	0.6	0.1
553	Deansway	Vessel foot	66.3	2.7	1.0	10.7	0.1	0.1	0.1	0.8	0.2

All of these antimony bronzes may have been smelted from *fahlerz* ores, tetrahedrite and tennantite $(Cu,Fe)_{12}(As,Sb)_4S_{13}$ which are well-known from Cornwall and Germany (Blair *et al*. 1986). The copper smelted from these sources would contain substantial proportions of arsenic and antimony unless great efforts were taken to remove them (Yazawa & Azakami 1969). Such an alloy would be unsuitable for many uses: it would be too brittle for the manufacture of sheet or wire. However, such an alloy would have a low melting point which would make it ideal for casting. Werner has suggested that these antimony bronzes may instead have been formed by mixing copper with *speiss* (a by-product of smelting complex non-ferrous ores, such as *fahlerz* ores) which has a variable composition but usually contains substantial amounts of antimony and arsenic (Werner 1976). However, analyses of *speiss* usually show relatively high iron contents (Werner 1976: table 2; Bachmann 1982: 29) which are not seen in the antimony bronzes analysed for this report, or in those analysed by Blades (1995).

There are many potential sources for the antimony bronze cast at Head Street. Relatively little copper was mined and smelted in Britain in the late medieval period and most copper appears to have been imported from the Continent (Blair *et al*. 1986). During the 16th century German miners were brought over to England but large scale working did not commence until the end of the 17th century (Crossley 1990: 197–8). During this period large quantities of copper were mined and smelted in Germany, and antimony bronzes were exported (Werner 1976). The recovery of large quantities of 16th and 17th century German stoneware from the site (Crummy *personal communication*) may support the idea that the antimony bronze was imported from Germany.

Conclusion

The composition of the spilt metal and the metal droplets in the slag is consistent with the manufacture of vessels, and cannot be used to support the suggestion that bells were being cast. Examination of the 13,000 13th to 16th century mould fragments and spilt metal from the Bedern foundry in York indicated that the principal products were small cauldrons (Richards 1993). Nevertheless, the main products of bell founders were often 'cauldrons and skillets . . . and these vessels accounted for the vast majority of the discarded mould material [in Exeter]' (Blaylock 1996: 72).

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