Metal to mould: alloy identification in experimental casting moulds using XRF

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ABSTRACT: Archaeological moulds are often analysed for metal traces to identify the alloys cast in them. However, the relationships between an alloy and its corresponding trace on a mould are not simple, and few studies have investigated them. This paper reports experiments in which copper alloys of known compositions were cast in clay moulds. The moulds were analysed using energy-dispersive X-ray fluorescence to determine the remains different alloys left in them. Some metal oxides mechanically adhere to the mould, but their different thermochemical properties ultimately determine the extent to which they become chemically bonded to the fabric. The metals behave differently in the presence of one another, determining which of the constituents of particular alloys leave traces. Inferences can be made as to the original alloys cast in moulds, but any conclusions should be drawn with caution.

Introduction

Crucibles and moulds used for casting metal objects are often the only remains indicative of metalworking found on archaeological workshop sites. Previous studies aiming to determine the types of metal melted in crucibles or cast into moulds have highlighted the many problems associated with the accurate identification of the metals being used (*eg* Barnes nd; Tylecote 1980, 204; Bayley 1989; Bayley *et al* 1991; Wilthew *et al* 1991; Dungworth 2000). One of the main problems is that the relative proportions of metals or oxides detected in a crucible or mould may differ from those of the original melt, hence the need for caution when interpreting any analytical results (Barnes nd; Dungworth 2000, 83).

Barnes' pioneering study was multi-faceted and included a survey of different types of moulds from a museum collection, and the experimental casting of bronzes and brasses into clay moulds. Through his experiments, he aimed to recreate the various residues and stains observed in archaeological examples, which were subsequently analysed by surface X-ray fluorescence spectroscopy (XRF). One of the first issues that he noted was the high amounts of zinc detectable in the moulds, even after casting brasses containing only 5% zinc or less. A similar pattern was seen for lead, while copper and tin were barely detectable. These observations, however, were not quantified.

More recently, Dungworth (2000) raised a note of caution on the analyses of crucibles and moulds, based on his study of crucibles from Mucking, Essex (Dungworth and Bayley 1999). Noting a significant mismatch between the composition of a metal prill trapped within a crucible and the relative proportions of the metal oxides detected in the same crucible fabric, he pointed out the main factors likely responsible for this: the melting regime, and the different volatilities and free energies of oxidation of the various alloying constituents. Dungworth's study, however, was based on the analysis of a small number of archaeological finds which did not allow him to test all of his hypotheses, or to investigate the existence of systematic patterns.

The current study sought to build on this previous work by conducting experimental casts of a range of alloys of known composition, and subsequently analysing the moulds, thus enabling clearer comparisons between the original alloy and the contamination in the moulds.

Table 1: Nominal compositions of the metals cast in the experiments, and the alloy names used to describe them.

Melt	%Cu	%Zn	%Sn	%Pb	Alloy aame
1	80	20	-	-	Brass
2	95	5	-	-	Brass
3	80	-	20	-	Bronze
4	95	-	5	-	Bronze
5	90	5	5	-	Gunmetal
6	80	10	-	10	Leaded brass
7	80	-	10	10	Leaded bronze
8	85	5	5	5	Leaded gtunmetal

Ultimately, the question was simple but of broad relevance: can we infer the composition of the metal cast in a mould, based on the analysis of that mould?

Research design and methodology

A variety of copper alloys were used in antiquity. Common ones, and the names assigned to them, are given in Table 1. Our experiments used these particular alloys, which had compositions ranging from lightly (5%) to heavily (20%) alloyed copper (Table 1).

The experiments

Initial experiments were conducted during the UCL Institute of Archaeology's experimental archaeology course based at Michelham Priory in 2003–5 (Kearns 2005). They were later repeated under laboratory conditions in the UCL Institute of Archaeology's Wolfson Archaeological Science Laboratories; the data presented here comes from this second set of experiments.

Industrial kaolinitic clay, tempered with ~30vol% quartz sand, was used for the moulds. The 'object' cast was in all cases a simple disc 35mm in diameter and approximately 5mm thick (Fig 1). These moulds were left to dry at room temperature for several days. They were not fired or preheated prior to use.

The metal charge used for each casting was prepared from industrial-grade pure metals (cut fragments of copper piping, zinc and lead sheet and tin wire) to produce the desired alloys; crucible charges ranged from 550–700g. The nominal, *ie* weighed-out, composition of each alloy was recorded prior to melting in laboratory standard clay-bonded graphite crucibles using an electric furnace at *c*1200°C. A new crucible was used for each melt to avoid cross-contamination. Each alloy was cast into three different moulds to assess consistency and reproducibility of the patterns observed. In addition, it was hoped that this might produce information on the relationship between casting temperature and mould contamination as the alloy temperature decreased during casting from Mould 1 to Mould 3. Overall eight different alloys were cast using twenty-four moulds.

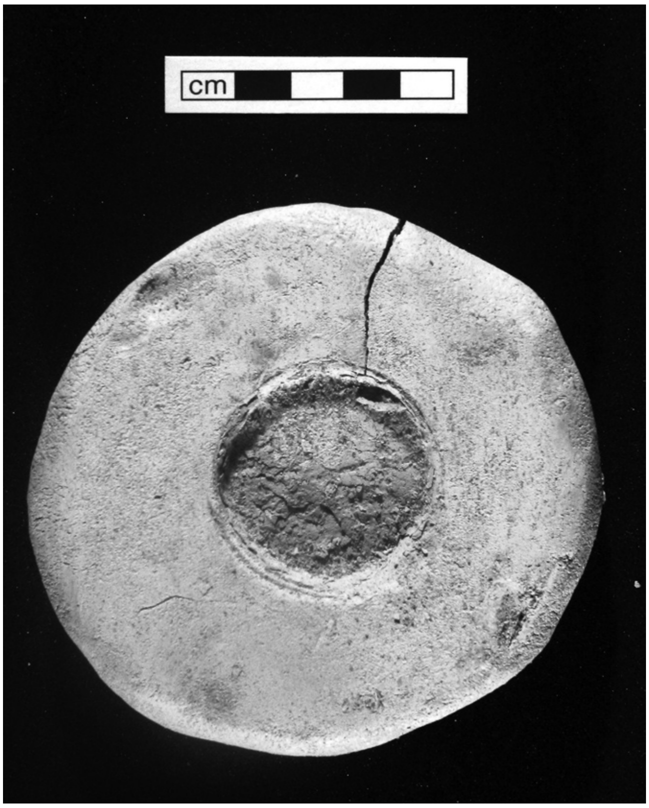


Figure 1: Example of a mould used in the experiments.

XRF analyses

After casting and removing the metal blanks, the moulds were then analysed non-destructively using energy-dispersive X-ray fluorescence (ED-XRF) in a Spectro X-Lab Pro 2000 instrument. The manufacturer-installed Turboquant method was selected, employing three secondary targets at accelerating voltages up to 40 keV for approximately 20 minutes. Turboquant is a generic method developed for the analysis of a wide range of materials including soils and oxide-based materials, combining fundamental parameters and empirical calibration values taken from certified reference materials. It is optimised for analytically ideal flat and homogenous sample surfaces; neither condition was met by our sample set. Despite this constraint on analytical accuracy and overall data quality, ED-XRF was deemed the most appropriate method of conducting a semi-quantitative chemical analysis of the moulds while ensuring that they would remain undamaged, thus making the method applicable to archaeological artefacts where the integrity of the artefact must be maintained. The deviation from the analytically-ideal surface quality would be shared by all samples making the data at least internally consistent and hence sufficient for the current study. The diameter of the area analysed was *c*15mm, which made it convenient to analyse a relatively large area centred on the area of the mould where the metal was cast.

The good sensitivity of most XRF instruments makes it possible to detect transition and heavy metals in silica-rich matrices at concentrations of 10ppm or even less. The more common base metals, such as copper, zinc and lead, are often present at much higher concentrations in clays and soils, easily reaching 50–100ppm, which reflects the common occurrence of these metals in the natural environment. This needs to be taken into account when looking for low-level contamination from a particular metallurgical activity. Thus, both the inner and outer surfaces of the moulds were analysed, as is common practice with archaeological moulds, in order to compare the composition of the 'clean' outside to that of the 'used' inner surface. (From now on, we refer to the use-related traces on the mould surfaces as 'contamination'.) A few unused moulds were also analysed. Each analysis was repeated three times in order to monitor precision. Having checked the internal consistency of the three analyses performed on each surface, it was decided to use average results in order to simplify data handling and presentation.

Based on the analyses of uncontaminated outer mould surfaces, an initial threshold level of 60ppm for copper, zinc and lead was defined as the 'natural' metal content in the moulds; only data above this was considered contamination from the casting experiments. For tin, the natural threshold was much lower and was defined here as 20ppm. However, the values for some of these elements occasionally appeared higher when the inner surfaces of the moulds were analysed, even if they were unused moulds or, if used, when the metal in question was not part of the alloy that had been cast in the mould. This is probably related to the poorer analytical geometry of this side of the mould, which was necessarily further away from the detector window.

The four elements of major interest, copper (Cu), zinc (Zn), tin (Sn) and lead (Pb), were typically detected in trace or minor concentrations, although in a few cases ranging up to several weight percent. Given the uneven geometry of the inner surfaces of the moulds, the analytical totals for the XRF analyses of these were variable, ranging from 6 to 85% and typically around 20%. In order to make the data internally comparable, all the results were initially normalised to 100%. Unavoidably, as with real archaeological artefacts, the data thus acquired is semiquantitative at best. For this reason, we have chosen not to report absolute compositional values as ppm, which might convey an impression of unrealistic accuracy levels. Instead, the discussion will focus on the relative proportions between the four elements of interest. The analytical values for Cu, Zn, Sn and Pb in the moulds were therefore normalised to each other and are expressed as percentages of their combined total presence, so that their relative proportions can be more directly compared to those in the original alloys cast.

Table 2: Summary of the thermochemical properties of the metals used in the experiments.

	Cu	Zn	Sn	Pb
Vapour pressure	low	very high	low	high
Free energy of oxidation	low	high	medium	low
Reactivity with silica	very low	yes	very low	yes

Thermochemical behaviour of metals

In agreement with Dungworth (2000), our departure point was the assumption that the contamination left on the moulds by metallic elements is dictated by their thermochemical behaviour. On this basis, the experimental results are discussed with reference to three factors (the vapour pressure, free energy of oxidation and reactivity with silica of each metal), and their relative influence on the contamination left in the moulds is assessed. A summary of relative values of these variables for the three elements/oxides discussed in this paper is presented in Table 2.

Vapour pressure/volatility

The vapour pressure of a metal is the pressure of the vapour evaporated from it at a given temperature. As such, it is an indication of the metal's evaporation rate. Elements with a higher vapour pressure are more volatile. Table 3 shows the vapour pressure for pure metallic elements at 1000°C. Data for the vapour pressures of alloys is not available, but the values for the pure elements are different enough to provide an indication of the varying volatility of the four elements studied

Table 3: Vapour pressure of metallic elements at 1000°C (after Brandes 1983, Table 8–13; as cited by Dungworth 2000).

Metal	Vapour pressure (mm Hg)
Zinc	4064*
Lead	4.91
Copper	3.5×10^{-4}
Tin	8.7×10^{-4}

Note: * the value for zinc gas extrapolated as data is only available up to 727°C

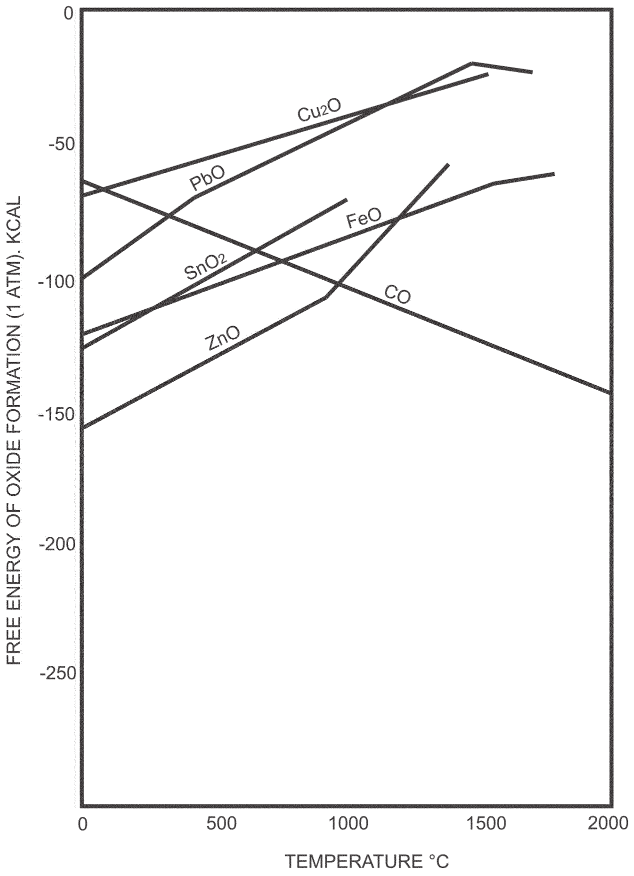


Figure 2: Ellingham diagram showing the free energy of formation of common metal oxides from the corresponding metal over a range of temperatures. The free energy of formation of carbon monoxide is also shown (redrawn after Killick 2001, 487).

at a temperature comparable to those employed in the casting experiments.

Table 2 shows that zinc has by far the highest vapour pressure, making it the most volatile of the metallic elements considered here. The vapour pressure of lead is considerably lower than that of zinc, but still much greater than those of copper and tin. While the high volatility of zinc, and to a lesser extent lead, could result in losses through evaporation during casting, it can also result in a stronger interaction with the mould fabric, resulting in greater levels of contamination reaching deeper into the mould.

Free energy of oxidation

Not all elements have the same predisposition to oxidise; metals with a greater tendency to remain in the elemental state are said to be nobler. This is illustrated in the Ellingham diagram, where the free energies of oxidation for different metals are plotted for a range of temperatures (Fig 2). The lower the line in the figure, the more likely that oxidation will take place at a given temperature.

A starting assumption was that those alloy constituents more likely to oxidise would be more likely to leave durable contamination in the moulds. This was based on the fact that oxides have lower surface tension and higher chemical reactivity than the corresponding metals, and hence they could be expected to more easily develop chemical bonds with the ceramic material than the metals themselves.

After casting, the metal remains liquid for a limited time, depending primarily on the size of the casting, the temperature of the metal and the mould, and the freezing range of the alloy. This is the main period during which oxidation takes place, *ie* before the artefact is removed from the mould. Assuming a casting temperature of *c* 1100ºC, it is clear that zinc would be most prone to oxidation, followed by tin. The values for copper and lead are significantly lower, making them less likely to oxidise.

Chemical reactivity with silica (SiO_2)

As the mould fabric consists primarily of silicates, either as clay minerals or quartz (SiO_2), it is important to consider how the various metal oxides react individually, and in the presence of each other, with these ceramic oxides. Here we use the reactivity with silica as a proxy for reactions not only with quartz but also with other silicates such as clay minerals. The formation of metal silicates can be illustrated by phase diagrams. As these diagrams are produced under controlled conditions and with pure reagents once equilibrium has been reached, they do not reflect exactly the situation of the reactions in the mould. However, despite this, they provide a good indication of the reactivities of the different metal oxides with silica, and therefore of whether they are likely to form chemical bonds. This reactivity is directly relevant for the stability of the bond between the metal oxide and the mould surface. Other factors relevant for archaeological moulds, but not measured in our experiments, are the resistance of the various phases to chemical attack during long-term burial, as well as the potential alterations through vigorous washing of moulds after retrieval.

The SiO_2-ZnO phase diagram (Reser 1969, fig 302) shows the phases formed by zinc oxide and silica at temperatures higher than 1300ºC, *ie* outside the range relevant to our casting experiments. However, analyses of archaeological crucibles employed in brass metallurgy have illustrated that crystalline zinc silicates and zinc-rich glassy layers can form in technical ceramics at temperatures around 1000ºC, even when only small amounts of zinc oxide are present (Martinón-Torres and Rehren 2002).

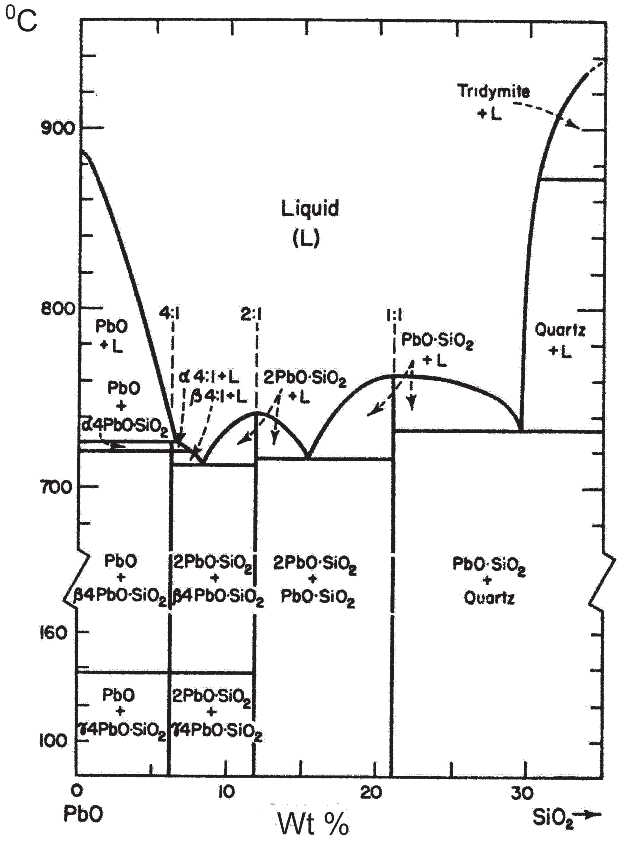


Figure 3: Phase diagram for PbO-SiO_2 (after Reser 1969, fig 284).

The SiO_2-PbO diagram (Fig 3) illustrates that even at relatively low temperatures, lead oxide reacts readily with silica and tends to form stable compounds. This phenomenon has been exploited for centuries for the deliberate manufacture of lead-silica glazes on ceramics (*eg* Tite *et al* 1998), and it can also be documented as an unintended occurence on the surface of ceramic scorifiers where metallic lead was oxidised in order to refine silver (*eg* Mongiatti *et al* 2009). Accordingly, one can expect lead to leave more traces of contamination in the siliceous mould than less reactive metals, particularly when cast under oxidising conditions.

In the SiO_2-CuO system (Fig 4), no reaction occurs between copper oxide and silica at temperatures below 1025°C. Therefore, even if copper oxide forms during casting, this will be unlikely to react with the mould as no chemical bond can form.

Finally, we have been unable to find a phase diagram for the SiO_2-SnO_2 system, and we can only assume that little or no reaction occurs between these compounds at the relevant temperatures. Although the analysis of tin-smelting slag demonstrates that high amounts of SnO can dissolve in a silicate glass (Chirikure *et al* 2010), the casting of bronze under oxidising conditions would probably promote the formation of SnO_2 rather than SnO. The fact that nearly pure SnO_2 crystals are commonly found in bronze-making slags (Rovira 2007) indicates the low tendency of this oxide to form more complex chemical bonds in the presence of silica. Therefore, as with copper oxide, we note the chemical reactivity with silica as very low (Table 2). Accordingly, if chemical reactivity is a driving factor in the mould contamination, tin could be expected to form discrete tin oxide particles, but no complex compounds, and therefore leave less contamination than more reactive oxides.

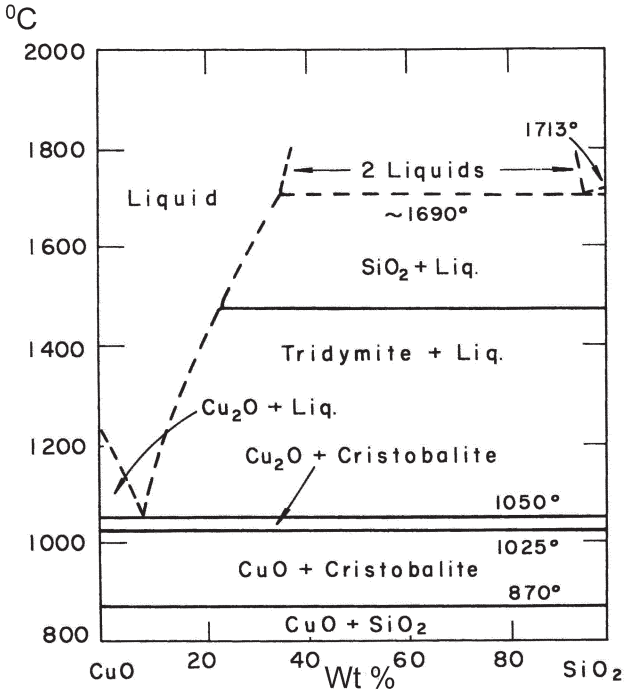
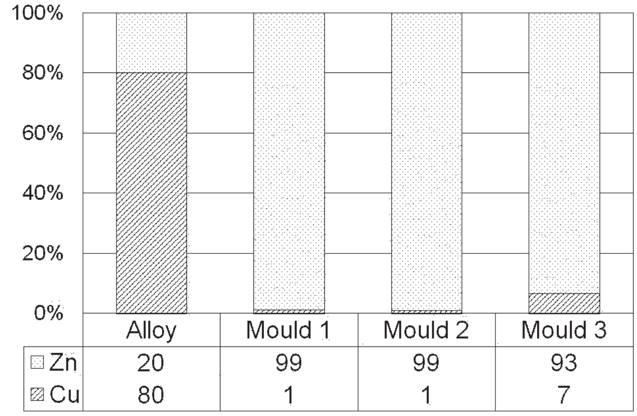


Figure 4: Phase diagram for CuO-SiO_2 (after Reser 1969, fig 2142).

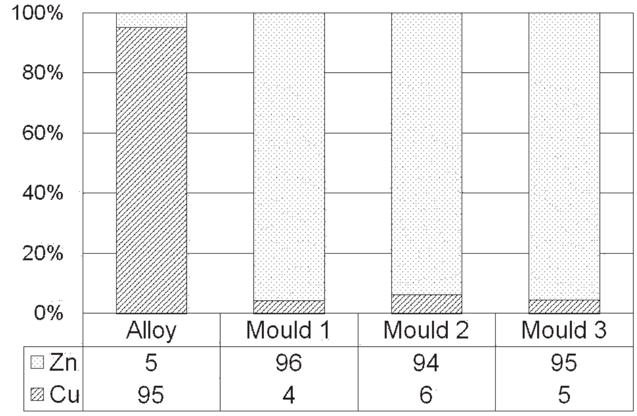
Results and discussion

Figures 5–12 provide a summary of the analytical results for each experiment. In general the results tend to show the same pattern for the three experimental castings made with the same compositional batch, which reinforces the validity of the observations presented below. Although in all cases Mould 1 received hotter metal than Mould 3, no systematic differences were noticeable from Moulds 1 to 3. It therefore appears that the casting temperature did not have a significant impact on the amounts (data not shown) or relative proportions of metals in the contamination left in the moulds, at least in these relatively small objects. The situation might be different if larger objects had been cast, and/or where there are larger temperature ranges between the casting and freezing points of the alloys.



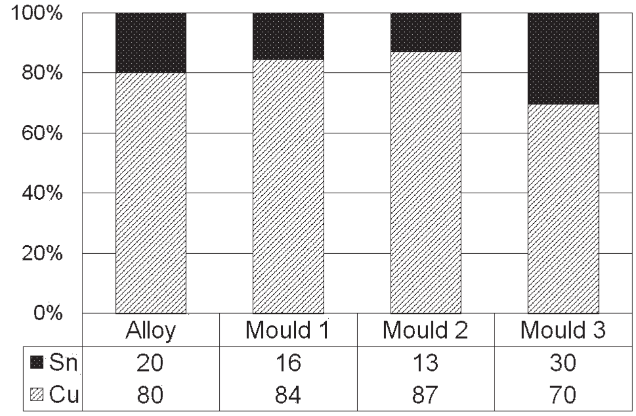
	Alloy	Mould 1	Mould 2	Mould 3
□ Zn	20	99	99	93
▨ Cu	80	1	1	7

Figure 5: Bar chart showing the composition of the 80:20 brass and the relative proportions of zinc and copper in the contamination in the moulds in which it was cast. The normalised values of the data plotted in Figures 5–12 are given in the table beneath each figure.



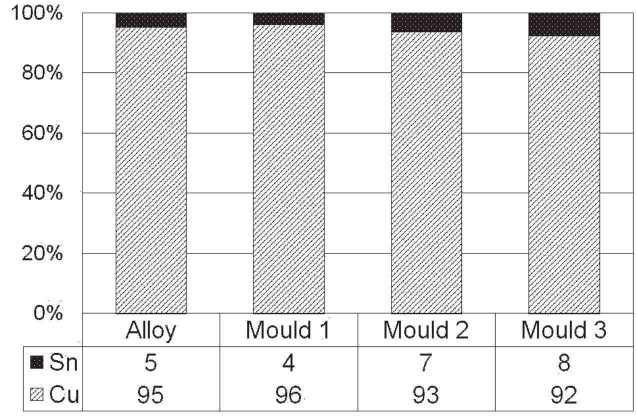
	Alloy	Mould 1	Mould 2	Mould 3
□ Zn	5	96	94	95
▨ Cu	95	4	6	5

Figure 6: Bar chart showing the composition of the 95:5 brass and the relative proportions of zinc and copper in the contamination in the moulds in which it was cast.



	Alloy	Mould 1	Mould 2	Mould 3
■ Sn	20	16	13	30
▨ Cu	80	84	87	70

Figure 7: Bar chart showing the composition of the 80:20 bronze and the relative proportions of tin and copper in the contamination in the moulds in which it was cast.



	Alloy	Mould 1	Mould 2	Mould 3
■ Sn	5	4	7	8
▨ Cu	95	96	93	92

Figure 8: Bar chart showing the composition of the 95:5 bronze and the relative proportions of tin and copper in the contamination in the moulds in which it was cast.

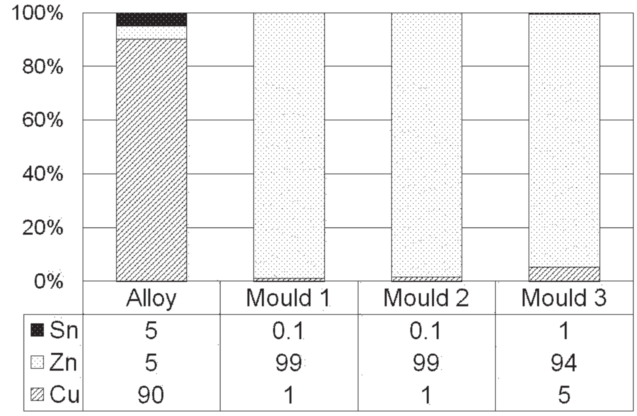
Brass

Two sets of brasses were cast, with Cu:Zn ratios of 80:20 and 95:5 respectively. The analytical results show that zinc becomes heavily enriched relative to copper in the mould fabric, even when as little as 5% is present in the alloy cast. This can be seen most clearly in Figures 5 and 6 where copper seems barely detectable in the moulds even though it was dominant in the alloy. It is worth noting that mould 3, used for 80:20 brass, shows the lowest Zn:Cu ratio in the contamination. This indicates that a higher zinc content in the alloy does not necessarily lead to a higher Zn:Cu ratio in the mould.

It is not surprising that zinc appears so heavily enriched if we consider its high volatility and free energy of oxidation, together with the chemical reactivity between zinc oxide and the silicates of the clay at high temperatures. In contrast, copper has much lower vapour pressure and rate of oxidation, and its oxide has a very limited reactivity with silica (see Table 2). Thus, when taken at face value, the analyses of comparable archaeological moulds could lead to the wrong assumption that particularly zinc-rich brasses were being cast. This is an important observation, as the zinc content of archaeological brass is considered a clue to its production technique, and it has been suggested that it could be used as a chronological indicator (Welter 2003). Likewise, crucibles or moulds with high zinc levels might be misinterpreted as related to intentional brass metallurgy, whilst the zinc content in the original alloy might have been small and unintentional. From our experiments it appears impossible to estimate the amount of zinc present in an alloy based on the surface analysis of a mould. It is notable that there appears to be no clear correlation between the zinc content of the alloy and the proportion of zinc found in the mould.

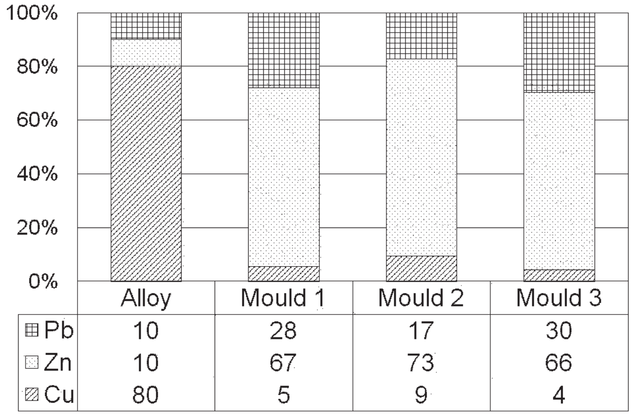
Bronze

Two sets of bronzes were cast, with Cu:Sn ratios of 80:20 and 95:5, *ie* directly comparable to the experimental brass compositions. The results, however, show



	Alloy	Mould 1	Mould 2	Mould 3
■ Sn	5	0.1	0.1	1
☐ Zn	5	99	99	94
▨ Cu	90	1	1	5

Figure 9: Bar chart showing the composition of the 90:5:5 gunmetal and the relative proportions of tin, zinc and copper in the contamination in the moulds in which it was cast.



	Alloy	Mould 1	Mould 2	Mould 3
⊞ Pb	10	28	17	30
☐ Zn	10	67	73	66
▨ Cu	80	5	9	4

Figure 10: Bar chart showing the composition of the 80:10:10 leaded brass and the relative proportions of lead, zinc and copper in the contamination in the moulds in which it was cast.

a different picture (Figs 7 and 8). In the moulds used for bronze, copper contamination predominates, while tin contamination is extremely low. Although a correlation can be seen between higher-tin bronzes being cast and a higher Sn:Cu ratio in the contamination on the moulds, the low overall levels of metals detected would make it difficult to infer this if the moulds were real archaeological finds. In fact, notwithstanding the relatively-low accuracy of the analyses, it is worth noting that the contamination in these moulds was much lower overall, and in some of them the tin content was barely above the threshold level of 20 ppm, *ie* tin was only present in concentrations comparable to those in unused moulds.

These results reflect the fact that tin, like copper, has a very low vapour pressure (Table 2). One might expect, however, that as tin is less noble than copper there would be enhanced levels of tin in the contamination on the mould. That this is not the case may be explained by the very low reactivity between silica and tin oxide, which counters any possible chemical bonding between the clay and the metal as it oxidises. If these factors were not taken into consideration, one might conclude that these moulds were used for casting artefacts of pure copper. A relevant example where this observation might become important is in prehistoric metallurgy where a common focus of research is the transition from the use of pure metals to alloys, the related understanding of the properties of different alloys, and the identification of workshops adopting the new alloy, bronze, early.

Gunmetal

A copper alloy containing equal amounts of tin and zinc (90:5:5) was cast. The levels of tin detected in the moulds were extremely low, and thus any of the three experimental moulds could have been interpreted as brass-casting moulds if they were archaeological finds.

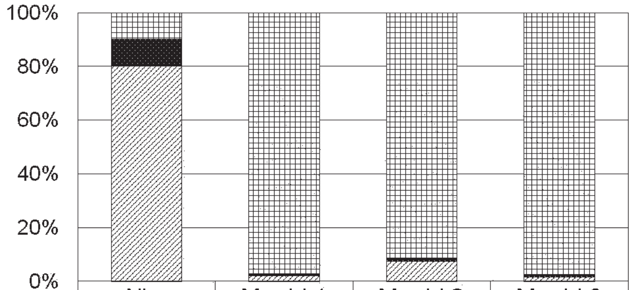
While copper dominates the alloy, it is again zinc which becomes most heavily enriched in the moulds (Fig 9). The properties of these three metals discussed above can explain this pattern (Table 2). In particular, the preferential reaction of zinc with oxygen inhibits the oxidation of tin, thus reducing even further the possibility of this metal leaving any contamination. The misidentification of moulds used to cast gunmetals as brass-casting moulds could trigger erroneous archaeological interpretations. For example, based on the analysis of metal objects, it is generally accepted that gunmetal replaced brass as the alloy of choice in late Roman times (Caley 1967; Dungworth 1996; 1997), and wrongly-interpreted results from archaeological moulds or crucibles could lead to the mis-identification of brass casting.

Leaded Alloys

The addition of lead to a copper alloy lowers its melting point and also increases its fluidity, which is useful when casting complex shapes. Lead may be present in high concentrations in archaeological alloys of mixed composition, and is often interpreted as resulting from uncontrolled recycling of scrap metal, or the re-use of lead-rich desilvered copper or *caldarium* (Dungworth and Nicholas 2004).

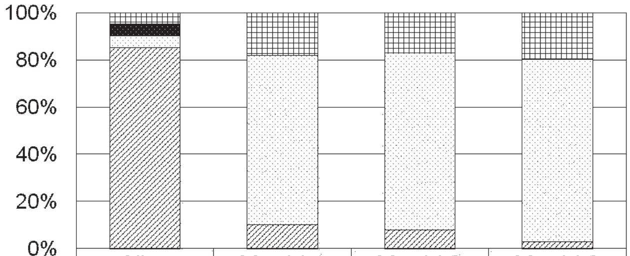
In these experiments, identical quantities of alloying additions were used so that their behaviour in the presence of each other could be assessed more systematically. Thus a leaded brass (80:10:10), a leaded bronze (80:10:10) and a leaded gunmetal (85:5:5:5) were cast.

While zinc and lead were present in the leaded brass in equal amounts, zinc follows the pattern noted above and becomes exceptionally enriched in the moulds (Fig 10).



	Alloy	Mould 1	Mould 2	Mould 3
⊞ Pb	10	97	91	98
■ Sn	10	1	1	1
▨ Cu	80	2	7	1

Figure 11: Bar chart showing the composition of the 80:10:10 leaded bronze and the relative proportions of lead, tin and copper in the contamination in the moulds in which it was cast.



	Alloy	Mould 1	Mould 2	Mould 3
⊞ Pb	5	20	18	20
■ Sn	5	0.04	0.05	0.08
□ Zn	5	78	80	79
▨ Cu	85	11	8	3

Figure 12: Bar chart showing the composition of the 85:5:5:5 leaded gunmetal and the relative proportions of lead, tin, zinc and copper in the contamination in the moulds in which it was cast.

Lead is also enriched to a substantial degree, in spite of its relative nobility which is comparable to that of copper (Fig 2). This suggests that volatility and chemical reactivity with silica are more important factors than the free energy of oxidation in determining the amount of contamination.

In the case of leaded bronze, all three metals in the alloy were detectable in the moulds, well above the threshold level of 60 ppm (Fig 11). Lead is enriched to the greatest extent but there are traces of copper and lower levels of tin. Most interesting is the tin contamination: although in relative terms it appears heavily diluted by lead, the absolute tin levels in all the moulds were much higher than in those found in the experiments with pure bronze, where tin was hardly detectable in the moulds (see above). An explanation for this may lie in the ability of lead oxide to promote the oxidation of other base metals and to form fusible compounds with them—a property routinely exploited when using lead to refine silver through cupellation (Bayley 1991). Furthermore, the lead oxide is likely to form a viscous glass phase which may facilitate the mechanical retention of tin oxide.

In the moulds used for leaded gunmetal, zinc once again predominates in the mould contamination, though only present in small quantities in the alloy; it is followed by lead, then copper (Fig 12). Tin is above threshold levels in all three moulds. Its relatively low concentration in the original alloy, and the greater affinity of zinc for oxygen, may explain the low levels of tin contamination in the moulds. However, even if low in relative terms, it is again worth noting that the absolute tin levels in the mould were higher than those detected in the moulds used for unleaded gunmetal (see above), again indicating that the presence of lead in the alloy enhances mould contamination by tin.

Summary, limitations and conclusions

The analysis of crucibles and casting moulds is often the only means of inferring the nature of the metals and alloys used for making objects in archaeological workshops. This study has shown that the relations between the alloys cast and the contamination left on moulds is systematic, but complex and difficult to predict. Zinc contamination will always appear at strongly-elevated levels in moulds, even if this metal is only present in the original alloy in small concentrations. Lead will also tend to be over-represented, although not as heavily as zinc. Tin, on the contrary, will leave very limited traces in the mould, sometimes close to limits of detection, even when heavily alloyed bronzes are cast. Traces of copper were detected in all the moulds analysed, although nearly always in relative proportions much lower than in the original alloys, often significantly so.

The different behaviour of the various alloying constituents may be explained in light of their thermochemical properties. Volatility appears to be the foremost factor, with more volatile metals such as zinc and lead consistently leaving more significant contamination levels. The free energy of oxidation is another important factor, as metal oxides are much more likely to be retained in moulds than the corresponding metals. In this regard, however, it is important to note that various alloying constituents behave differently in the presence of each other. In zinc-containing alloys, the highly-volatile and reactive zinc will tend to react preferentially with the limited oxygen available during metal cooling, thus effectively inhibiting the oxidation of the other metals present—and hence decreasing their likelihood of leaving contamination. This is particularly noticeable in the case of alloys containing both zinc and tin. In contrast, the presence of lead in an alloy will enhance mould contamination by all the other metals present. Thus tin leaves more traces of contamination when present in leaded alloys than when casting pure bronzes—although in relative terms it will be heavily diluted by the more volatile metals. We suggest that this may be related to the ability of lead oxide to promote the oxidation of other base metals forming complex, double-metal oxides that are more easily bonded to the mould surface.

Finally, the chemical reactivity between the mould material and the metal oxides that form is also an important factor affecting the levels of contamination that different metals will leave in clay moulds. The very limited reactivity between silica and both copper oxide and tin oxide makes it very difficult for these metals to leave traces, whereas the oxides of zinc and lead will readily form stable and relatively corrosion resistant silicates on the mould surface at the usual casting temperatures.

Only when these factors are considered and balanced can we begin to use analytical data from surface analyses of archaeological moulds to infer the compositions of the original alloys cast. Even so, based on present knowledge, these inferences should only be qualitative.

There are several limitations to this study, most of which could be addressed by further experimentation. For the time being, we can only make assumptions and suggest future lines of enquiry:

- *Use and re-use of moulds*
  Some archaeological moulds, particularly those made from stone, will have been used more than once, and sometimes with different alloys. If a mould is repeatedly used for the same alloy, we can expect the overall contamination to increase, but the relative proportions between elements may change due to the presence of metal oxides and silicates already on the mould surface when the casting is made. If the mould is used for different alloys, then the patterns of contamination are unpredictable and may be misleading.

- *Mould material*
  The raw materials in the experimental moulds were kept constant in order to allow internal comparisons, but different mould materials will behave differently and show different degrees of reactivity with the metal oxides. For example, clays richer in alumina, or heavily tempered with carbonaceous material, may be less reactive and therefore show comparatively lower traces of contamination than those richer in free silica.

- *Mould texture and surface finish*
  Smoother surfaces with few details will have less surface exposed to reactions, hence minimising the contamination. Another factor related to this is the use of a parting layer such as soot or powdered charcoal on the inner surface of the mould, as is sometimes apparent in archaeological examples. This layer would also inhibit oxidation and decrease the probability of traces being left in the moulds.

- *Mould shape*
  In closed moulds the oxidation will be lower, which would affect the contamination through oxidation. However, a closed environment would favour contamination by volatile metals. This phenomenon is noted, for example, in brass making and melting crucibles, were the fabrics of closed vessels systematically show higher zinc contamination than open ones (Martinón-Torres and Rehren 2002). However, caution should be exercised when making extrapolations from this study to crucibles, given their wide variety of materials and operating parameters.

- *Casting/freezing temperature*
  Our results suggested that there is no clear correlation between the casting/freezing temperature and the contamination in the moulds, either in the amount of contamination (results not shown) or in the relative proportion of the contaminants. However, our metal discs were all relatively small and solidified very quickly. It is likely that larger artefacts with longer freezing times would leave more contamination as there would be relatively more time for the contaminating reactions to take place. Factors would be the temperature of the metal melt and the size of the object being cast, but also the freezing point of the alloy and the temperature of the mould; preheated moulds, for example, would lead to slower cooling rates and thus probably increased contamination.

Much more work could be conducted in several areas, but the data reported here allows us to end with two conclusions. The bad news is a reaffirmation that we cannot make direct correlations between the traces detected in moulds and the metals cast in them. The good news is that, with caution and taking moderating factors into account, we can begin to make informed estimates of the metals cast in clay moulds, at least at a qualitative or comparative level. With the recent advent of relatively affordable, handheld XRF analysers, we will probably see an increase in the number of metallurgical ceramics analysed by this technique. It is hoped that the work reported here will facilitate and encourage more balanced interpretations of the resulting data.

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