Ancient Monuments Laboratory
Report 3/99

X-RAY FLUORESCENCE ANALYSIS OF IRON AGE METAL WORKING DEBRIS FROM WICK AVENUE, WHEATHAMPSTEAD, HERTFORDSHIRE

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Summary

The site produced fragments of moulds and crucibles used for the melting of bronze and silver and the casting of bronze linchpins or ferrules. It is speculated that the zinc content of the bronze may be from a copper ore containing zinc. Also identified were fragments of a triangular loom weight and other ceramics.

Author's address :-

Ms M Dennis
ENGLISH HERITAGE
23 Savile Row
London
W1X 1AB

X-Ray Fluorescence Analysis of Iron Age Metal Working Debris from Wick Avenue, Wheathampstead, Hertfordshire

Megan Dennis

Introduction

The site at Wick Avenue in Wheathampstead, Hertfordshire (national grid reference TL 175 134) was excavated by the Verulamium Museum in July 1998. It was discovered during building work. After the recovery of a human skull, work was delayed whilst a rescue excavation took place. A female human burial was found in a ditch amongst a rubbish deposit. At the feet of the woman several fragments of metal working debris was uncovered including fragments of mould, crucible, metal waste and slag. Among this deposit the partial skull of a baby was also discovered. The site has been dated to between AD 10 - 40 from the typology of the pottery finds. All the metal working debris was recovered and the assemblage as a whole weighs only 626 g. The fragments represent a variety of different types of artefact and to identify the alloys used in these objects analysis by X-ray fluorescence was undertaken.

Background

The Iron Age was a time of innovation for metal working with many publications studying the processes and raw materials behind the finished objects (for example Spratling, 1979 and Tylecote, 1986). Bronze (an alloy of copper and tin) was introduced into Britain in around 1800 BC (Savage, 1968, 30) and was in wide use for a large number of objects until the emergence of iron from the continent in 7th century BC (Megaw and Simpson, 1979, 382). Gradually, bronze began to take a less functional role being used for decorative and ornamental pieces while iron, and particularly steel, being less malleable and harder, was used for tools and weapons. Castings became increasingly complicated and this may be one of the reasons that as the Iron Age progressed bronzes tended to have an increasing percentage of lead within them. Lead considerably improves the casting qualities of an alloy (Blades, 1995, 34), making it easier to handle and produce intricate items. Silver is known to be used from the Early Iron Age, and probably before, mainly for jewellery and decorative pieces (Tylecote, 1986, 76). The silver would probably have been produced from argentiferous lead ores, such as galena (Tylecote, 1986, 58). On the continent during the Iron Age brasses (alloys of copper and zinc) and gunmetals (alloys of copper, zinc and tin) were beginning to be used (Tylecote, 1986, 35). The working of these alloys is very rare in the UK at this time, but trade items of this composition have been found on Iron Age sites in Southern England (Bayley, 1998, 10-11)

The technology involved in the casting of copper alloy artefacts changed little throughout the Iron Age - industrial assemblages from various sites (for example Gussage All Saints) often include crucibles, moulds, copper slag and waste (Megaw and Simpson, 1979, 382). There is rarely any structural evidence of copper alloy casting - the debris found is usually part of a rubbish deposit or thrown into a pit as at Gussage All Saints (Wainwright, 1979, 126). The metal working debris assemblage at Wick Avenue represents most of these categories of finds.

Description of the Debris

All the samples were visually examined. The assemblage can be separated into moulds, copper alloy waste and slag, crucible fragments, hearth lining and other debris.

Ceramic Moulds

Ceramic mould is a light, friable material with a high proportion of vegetable matter tempering. Through use the inside of the mould (the casting surface) becomes reduced (appears grey/black) and the outer edges remain oxidised (red/orange). This makes them easy to identify. Moulds for different types of object can also be identified if the fragments are large enough. In the assemblage from Wick Avenue there was a total of 110 g of mould fragments. The moulds would have been used to cast objects using the "lost wax" method. The fragmentary nature of moulds and the absence of mating surfaces (where one half of a piece mould lay against the other) allows their identification as investment ("lost wax") moulds. The process involved in making an object using the "lost wax" method was complicated. A wax model would have been made of the object required. Clay would then be placed around it to form the mould. The mould would have been fired, melting the wax out. The metal alloy for the object would then be poured into the space left where it would quickly solidify. When the alloy was completely cold the mould would be broken apart and the object removed and finished.

The moulds were of 2 types - those possibly used to cast linchpins for wheels and moulds where the object being cast was not identifiable.

The linchpin moulds were fragmentary, but from the surviving pieces it can be seen that there are at least 3, perhaps 4, moulds represented. 15 fragments of this type of mould were recovered. They weighed 86 g. The linchpin mould fragments were separated into three groups because there were three recognisable bases within the collection (see Figure One for mould A base). X-ray fluorescence analysis revealed that one of the other fragments was clearly identifiable as belonging with mould B, as both fragments contained no lead (see Table One). The other fragments could not be identified as belonging to mould A or C and so were grouped as mould A. XRF analysis was undertaken on all the fragments of linchpin moulds but results of only the bases are presented here. The other fragments within each group showed similar results to the base fragments.

The linchpin mould fragments were too small to enable full reconstruction. It can be seen that the objects cast would have been cylindrical with a series of ridges and lines running around them - a repeating pattern found on many of the fragments is a wide band followed by 2 narrower bands (see Figure Two). Linchpins often have a similar design and a decorative element on the flat end (for example Stead, 1991, 45, Figure 37 and 38 and Spratling in Wainwright, 1979, 135, Figure 101). This is missing on the bases from Wheathampstead, but the moulds are highly friable and the fragile original casting surfaces are easily damaged leaving a rough and uneven surface as is seen on these fragments. Measurement of the bases reveals that the items would have had a diameter, at the flat end, of about 25 millimetres, slightly larger than linchpins found in East Yorkshire in several cart burials (Stead, 1991, 44) but of similar size to one found in Beechamwell near Narborough, Norfolk and stored in King's Lynn Museum (Spratling, 1972). But the moulds may not be for linchpins. Similar lost wax moulds with a series of ridges and lines were also used for many other objects throughout the Iron Age (Tylecote, 1986, 35) including ferrules, spear butts and torque terminals.

Linchpins had three parts - two cast bronze terminals and an iron pin onto which they were fixed. Each part was made separately and then slotted together through the axle to stop the wheel falling off. Earlier linchpins may have been simple iron pins whilst the bronze decorative terminals were a later addition.

One of the linchpin moulds has a set of irregular striations running across the oxidised side of the two base fragments (see Figure One). It is unclear how they were formed - they are not textile imprints or deliberate decoration. They may have been caused by standing the newly formed mould, before firing, on straw, or scratching the soft unfired clay with a fingernail. As each linchpin had two terminals they would want to be kept together through production stages because they form a pair. The scratches on the bottom of the base may have been a way of identifying matching pairs - with the other terminal mould also having the same scratches on it.

The mould fragments used for casting unidentifiable objects (mould D) are very friable. The two colours of clay present (oxidised red and reduced grey/black) show the fired clay was from a mould but original surfaces only survive on the largest fragment. This fragment also appears to have traces of copper corrosion upon it. They fragments in this group have a different fabric type from the linchpin moulds being an orange crumbly and friable clay. There are 6 fragments of mould for the casting of unidentifiable objects which weigh 24 grams.

Copper Alloy Waste and Slag

This was a small group of tiny fragments in the dark layer found at the feet of the skeleton. It probably fell from the crucibles in the assemblage and became mixed into the surrounding soil matrix. This "dark layer" also included fragments of copper slag (also from the crucibles), charcoal, chalk, soil and tiny fragments of mould, crucible and other ceramic. These fragments were so small that it was impossible to separate them or analyse each one. Therefore the largest fragment was taken as a sample and analysed (see Table One).

Crucible Fragments

The crucible fragments were separated after the visual examination based on their fabric type, colour, oxidation or reduction of the ceramic, and copper alloy waste or other metal working deposits inside them. Three groups of fragments were formed - A, B and C. There were no complete crucibles in the assemblage. Crucible A was represented by a single fragment weighing 8 g. It had a black charcoal-rich deposit on the inner surface. It was relatively thin when compared to the other crucible fragments, being only 9 mm thick. It has a highly reduced clay, appearing black in colour, internally but had a less reduced (dark brown) outer surface.

Crucible B consisted of 27 fragments, but these were mostly small - only 111 g in total. They are made of highly vitrified reduced clay of a dark brown through to dark grey and black colour. Some original surfaces were retained on the fragments, and on some of these small areas of copper corrosion were visible. These also showed up on the X-radiograph. The fragments were similar in some respects to crucible C, but mostly smaller, less well defined fragments with little copper alloy waste on the remaining surfaces.

Crucible C consisted of 6 fragments of large flat-based crucibles similar to those found at Gussage All Saints (Spratling in Wainwright 1979, 132, Figure 99). The fragments weighed 161 grams. They included a large section of rim (see Figure Three) and also part of a thumb-pinched spout (see Figure Four). The fabric of the fragments is a grey reduced ceramic throughout, and some of them retain areas of copper-rich slag. These can be seen on the X-radiograph and by close visual examination, but as the pieces have not been cleaned or conserved are difficult to recognise immediately. A ceramic fragment and a sample of the slag contained in it were analysed by X-ray fluorescence.

Hearth Lining

Hearth lining fragments weighed 134 g and was made up of 3 large flat fragments. They had very slag-rich red reduced and vitrified inner surfaces and little remained of the outer clay except in some cases some very friable oxidised (orange) clay survived because it was attached firmly to the slag. The vitrification of the clay occurs after reaction at very high temperatures, such as those near a tuyere (hole through which air is pumped from the bellows into the hearth).

Other Debris

Ceramic A and B may not be directly linked to metal working. Ceramic A comprises 2 fragments of rich red oxidised clay. One may represent the rim of a vessel. There are no slag layers or metal traces, as found in some of the other debris, although there is some charcoal in the edge of the rim fragment. This may have become attached during burial, from the surrounding matrix. The fragments have been strongly heated.

Ceramic B is 3 fragments of very coarse red-brown ceramic with a reduced outer edge containing quartz inclusions up to 10 mm in diameter. One of the fragments has a hole punched, or pushed through it (see Figure Five). None of the inner surfaces remains. Closer examination of these fragments was required to try and identify them. Consequently the largest fragment was cleaned. The outer layer of soil was removed with a scalpel under a microscope and it was then gently cleaned with IMS (industrial methylated spirits) first with a brush and then dampened cotton swabs. After cleaning several striations could be seen on the inner surface of the hole. These show where an object (probably a stick) was pushed or pulled through the ceramic to form the hole before firing.

Analytical Method

X-ray fluorescence analysis of copper alloy and waste can distinguish between different copper alloys. Analysis of crucibles and moulds can identify the copper alloy used in them, if there are sufficient amounts of metals remaining.

X-ray fluorescence (XRF) analysis provides a non-destructive method of identifying the alloys present on the samples. It involves the excitation of atoms within the sample by X-rays. The atoms then give out characteristic X-rays of their own. The energy of these secondary X-rays identifies the elements present in the sample. Results are presented in graphical form with energy of the X-rays being plotted against number of X-rays of that energy (counts). Each element present will be represented by one or more peaks in the graph. Generally, the larger the peaks the more of that element is present in the sample. The results of the analysis were recorded as the height (in counts) of the peaks of interest within the spectrum: copper (Cu), zinc (Zn), lead (Pb), tin (Sn), antimony (Sb) and arsenic (As). Any other detectable peaks were also recorded. The counts are not directly proportional to the abundance of the elements present in the sample. They are also dependent on other effects produced within the sample (such as absorption of secondary X-rays), the shape of the fragment, its position within the XRF machine and the effects of burial conditions (Bayley, 1992, 817-8). Different metals also react differently in contact with the ceramic. For example unreactive elements such as silver or gold are not detectable unless they are trapped in the item as discrete drops of metal but lead and zinc are enhanced as they become chemically bound into slags, waste and ceramic. Therefore the identification of metal alloys requires careful interpretation of the results. In some cases no more can be stated than the object has been "heated in the presence of a copper alloy". The results for the samples analysed are presented in Table One.

Table One: XRF Analysis of Metal Working Debris from Wick Avenue, Wheathampstead

*** - strong signal
** - present
* - weak signal
tr - trace
? - identification uncertain

Context	Object/Group	Cu	Zn	Pb	Sn	Other Peaks	Alloy Identification
5	mould A	tr	tr	*			heated in presence of a copper alloy
5	mould B	tr	tr				heated in the presence of a copper alloy
5	mould C	*	**	***			heated in the presence of a copper alloy
5	mould D	***	*	***	**	As = tr	bronze
5	copper waste	***	***	**	***	As = *	bronze containing zinc
5	crucible A	*	*			Ag = *, Br = *	silver
5	crucible B	***	*	**	*	Ni = tr,	bronze
5	crucible C (slag sample)	***	***	***	*	Ni = tr	bronze containing zinc
5	hearth lining	***	***	***	***		bronze containing zinc
5	ceramic A	tr	tr				not a crucible
5	ceramic B	*	*				not a crucible

Discussion

The metal working debris at Wheathampstead shows that casting of copper alloy objects was occurring locally. The moulds have all been used to cast copper alloys. Moulds A, B and C were probably used to cast similar if not identical objects, probably linchpins or ferrules. Similar objects have been found in Iron Age graves in East Yorkshire (Stead, 1991, 44-47). There is evidence for the production of at least 3 linchpins from the fragments remaining - perhaps more. These objects did not, however, have the same alloy composition. Two of the moulds were used to cast an alloy containing copper, lead and zinc (moulds A and C) whereas the alloy on mould B did not contain lead. Lead is easily detectable because it is a heavy element and reacts with the ceramic. Therefore if the casting alloy had contained lead it would still be detectable in the mould. The traces of zinc found in the moulds is unusual for this period - brasses were not widely produced in Britain until after the Roman Conquest in AD 43 (Bayley, 1998, 10-11) and the few objects that do occur in Southern England are thought to be trade items from Gaul. It is possible, however, that trade items were being melted down and recycled into new objects, as the Trinovantes (based in North Essex and Suffolk) re-melted brass Roman coins to produce their own currency (Northover, 1991). The zinc in the Wick Avenue samples is not, however, of high enough levels to be a major component in the alloy. It is more probable that the copper ore being used to supply the copper for the alloy had a low natural zinc content. One published example of this is the ores at Llanmynech and Llyn Bryn-Dinas, north Powys (Northover, 1991, 210). The hillfort at nearby Breiddin has several bronze objects with detectable quantities of zinc in them (up to 3.76%, Craddock and Werner, 1991, 205-210). Because zinc is a volatile element it will be held within ceramic fabrics and reacts easily to form slags and therefore appear in much higher concentrations in analysis than was originally in the alloy. Ores from north Powys also contain traces of arsenic, nickel, iron and silver (Northover, 1991, 210-212). It can be seen from Table One that several of the objects had trace levels of arsenic, nickel and silver in them. This suggests the copper in the bronzes melted at Wick Avenue could have come from north Powys, though they could have come from other copper ore deposits that contain zinc and were exploited at this period.

The fragments of mould used to cast unidentifiable objects (mould D) may have come from one or several different moulds - they are too small to reconstruct. They were used to cast an object/objects of bronze. Bronze was a common alloy used during the Iron Age for many different items both decorative and functional - pins, brooches, wheel attachments, horse fittings, vessels and coins (Tylecote, 1986). It is impossible to say what objects these mould fragments were used to cast.

The crucibles provide evidence for the melting of two different alloys - bronze and silver. The zinc in the slag from crucible C is present because zinc reacts to form slag and is absorbed into the ceramic, whereas less volatile elements such as copper and silver do not. This means that any zinc in the alloy in the crucible shows up well in analysis, but copper and silver show less well. Crucible fragment A has high levels of silver and bromine (commonly present in silver corrosion products). Silver is a non-volatile element that is rarely detected by analysis unless retained as small droplets in the fabric of the ceramic. Therefore even the low quantities in this fragment must be evidence for melting of silver. The relatively high levels of copper and zinc in the fragment also show that this is a debased silver with other elements added to it. Such an alloy may have been deliberately used in preference to pure silver because it was cheaper and harder.

The hearth lining fragments are evidence of the melting of the metals on a small scale in a hearth. The lining itself only survives where it is vitrified in the area around the tuyere, where the bellows where the bellows feed air into the hearth. This area becomes a "hot spot" and so the clay becomes highly vitrified.

The copper waste found in the dark layer at the skeleton's feet gives further evidence for melting bronze containing some zinc. Because the fragments are so small it is probable that they fell from the crucible fragments that in some cases have a layer of copper waste adhering to their inside surfaces

Ceramic B is fragments of a triangular loom weight. These were in common use for domestic textile production throughout the Iron Age. They are made by forming a lump of clay into a triangular shape around a stick and then pulling it out. Alternatively the hole may be pushed through the clay after it has been formed. The ceramic is then fired. The low levels of copper and zinc detected in the ceramic fabric may be from close contact of the fragments with the metalworking debris in the assemblage (they all came from the same context).

Ceramic A is not connected with metal working. It has been heated after firing and may be part of a cooking vessel.

None of the fragments were severely abraded. This suggests that they were disposed of quickly after use and not left uncovered for very long. There are many details still evident on some of the mould fragments which are very fragile and usually degrade easily and quickly. It seems likely that they were part of the rubbish fill placed in the ditch over the burial.

Conclusion

The metal working debris from the burial at Wick Avenue, Wheathampstead shows that there was local casting of copper alloys to form linchpins and other objects. There was melting of bronze and silver. The copper used came from an ore which contained zinc, meaning the alloys produced from it also contained zinc at low levels. The debris was placed over the body soon after use, otherwise the mould fragments would be in a more deteriorated state.

Acknowledgements

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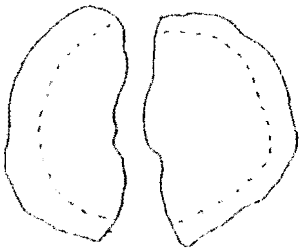
Diagrams

Figure One

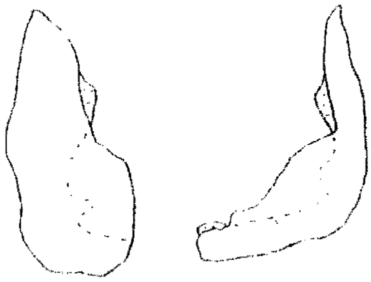
inside surface



2 matching fragments of base

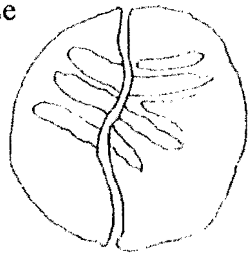
Mould A base fragments

sketch not exactly to scale



inside surface

striations on the outside of the base



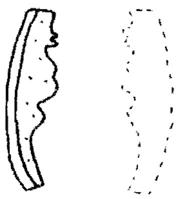
0 3 cm

Figure Two

Mould A fragment with band decoration

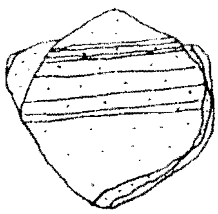
sketch not exactly to scale

oxidised clay



matching fragment from opposite side of mould?

reduced clay

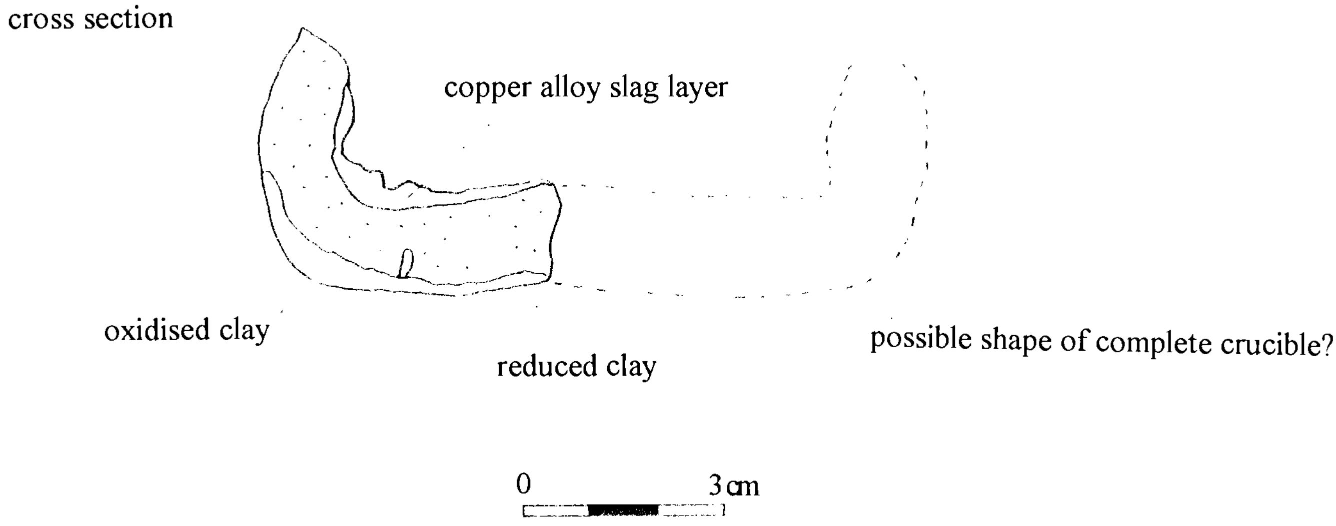


0 3 cm

Figure Three

Crucible D Flat Bottomed Crucible Rim

sketch not exactly to scale



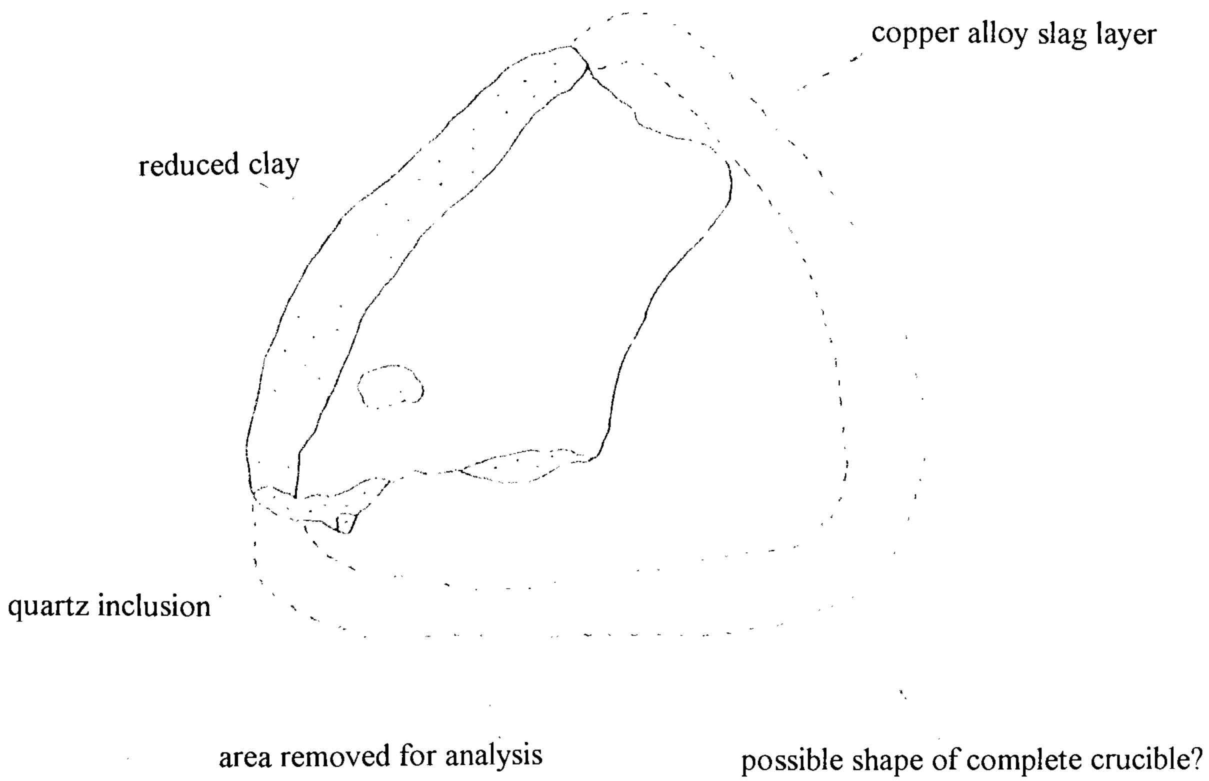
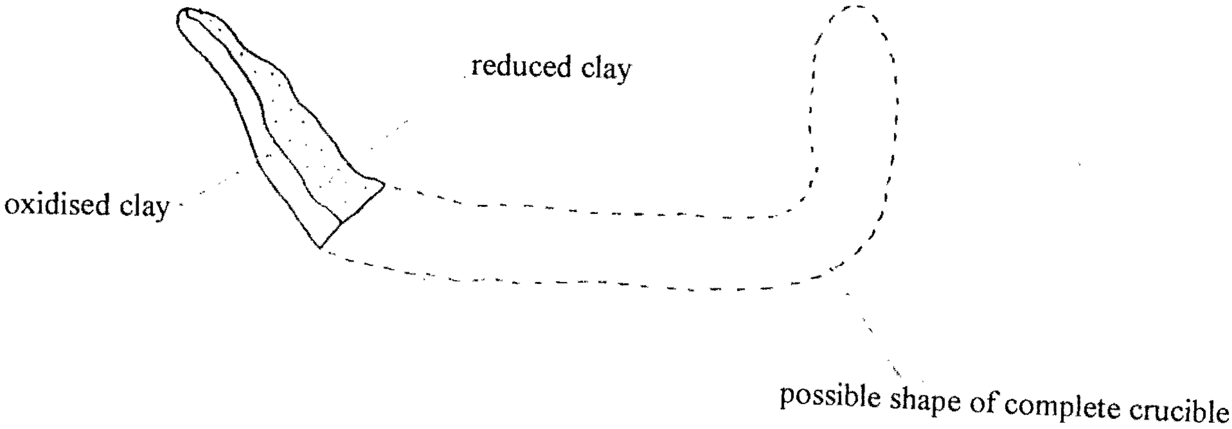
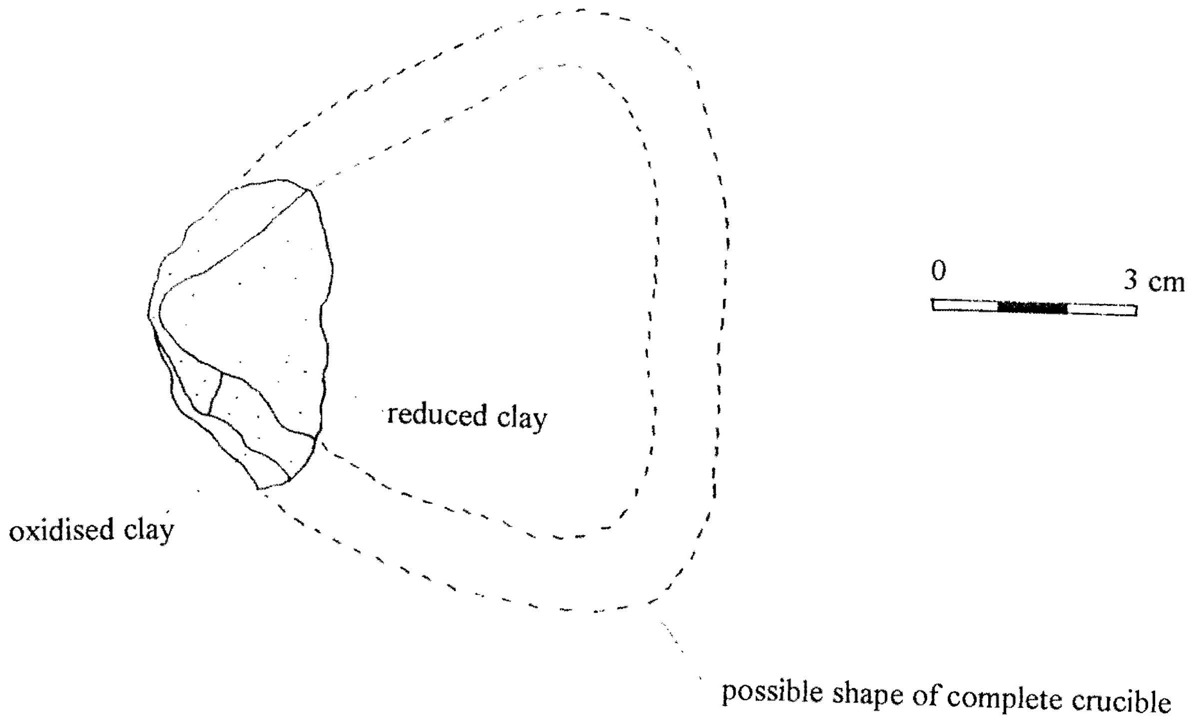


Figure Four

Crucible D Flat Bottomed Crucible Spout

sketch not exactly to scale





method of forming a thumb pinched spout

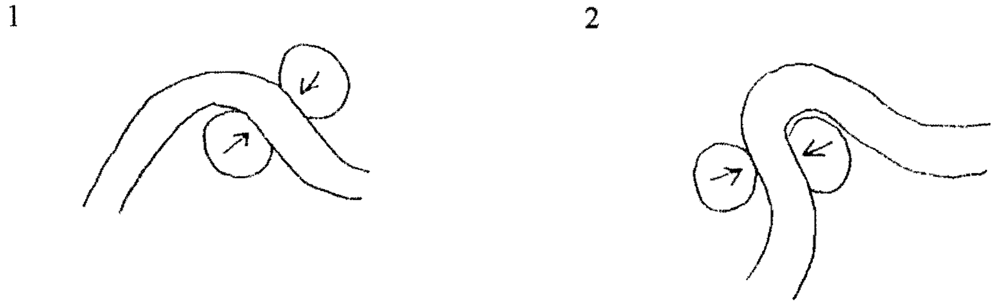


Figure Five

Ceramic B Punched Hole Fragment

sketch not exactly to scale