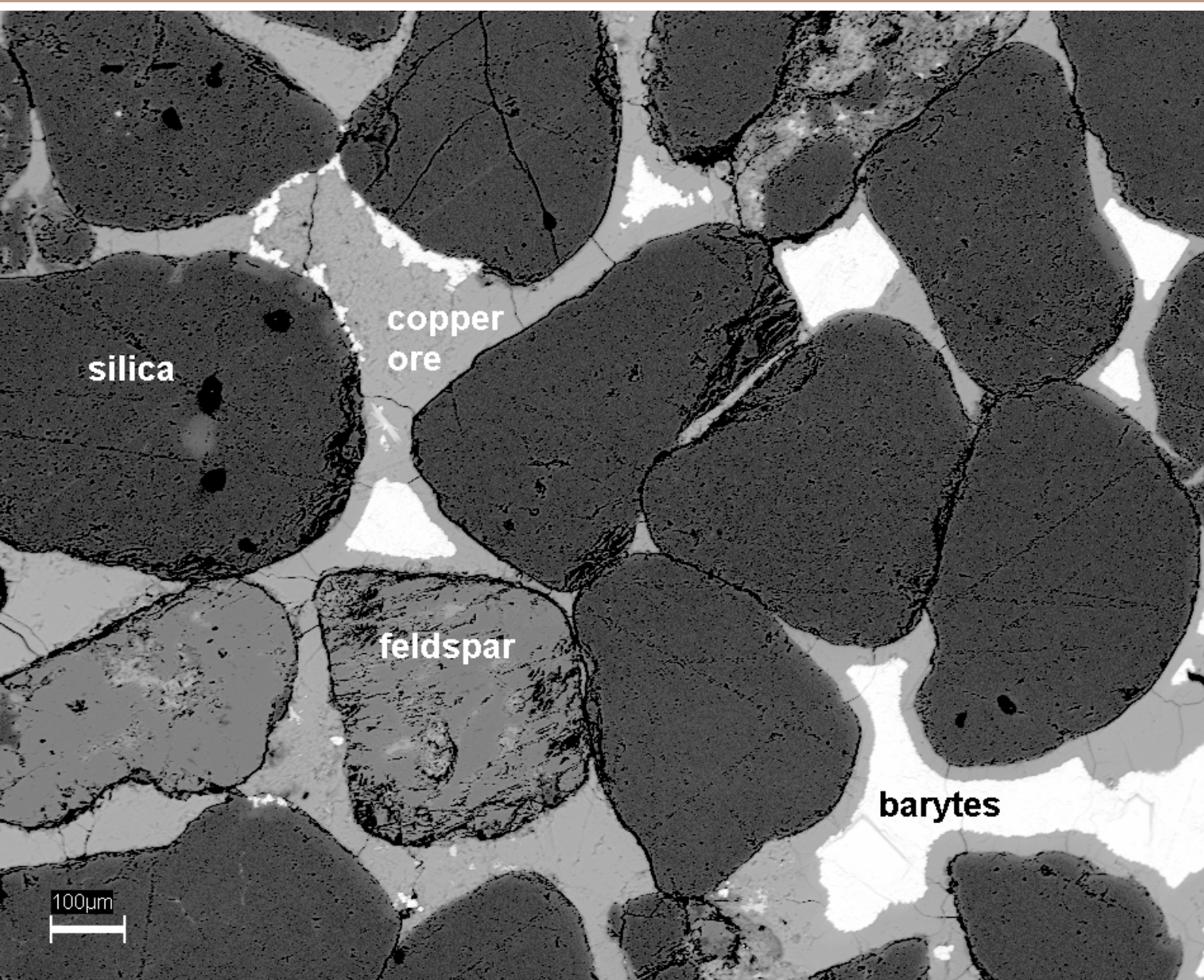


UPPER FORGE, COALBROOKDALE,
TELFORD, SHROPSHIRE
THE EXAMINATION OF CRUCIBLES,
COPPER ORE AND SLAG

TECHNOLOGY REPORT

David Dungworth, Paul Belford and Rob Ixer



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NGR: SJ 6689 0415

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ISSN 1749-8775

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SUMMARY

Excavations on the site of one of the earliest English steel cementation furnaces yielded materials likely to have been used in the production of copper and its alloys. Historical records indicate that during the first two decades of the 18th century Abraham Darby and partners were engaged in smelting copper and the manufacture of brass 400m to the north of the excavation. The materials examined were a sample of ore, a sample of slag and fragments from two separate crucibles. The examination of the ore suggests that it derives from the Permo-Triassic sandstones of Shropshire. The slag shows some compositional similarities with the ore but contains matte inclusions which suggests that the smelting was carried out using a mixture of ores. The crucibles showed elevated concentrations of zinc which may be due to them having been used for the manufacture of brass.

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DATE OF RESEARCH

2008–9

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INTRODUCTION

Recent excavations at Upper Forge, Coalbrookdale uncovered the remains of two 17th-century steel cementation furnaces (Belford 2003; Belford and Ross 2004; 2007). The excavations also recorded remains of a later malthouse and domestic housing. Several excavated contexts provided material evidence for the working of copper, comprising fragments of copper ore, copper slag and crucibles used for copper working. Although this copper-working evidence was not *in situ* and is probably residual in the contexts in which it was found, it is nevertheless potentially of great importance.

In 1702 Abraham Darby (with three partners) set up a brassworks at Baptist Mills in Bristol (Cox 1990, 128). 1706 Abraham Darby and other Bristol Quakers established a brassworks in Coalbrookdale and, at the same time (or possibly slightly later), Darby set up a copper smelting furnace in Coalbrookdale (Trinder 2000, 22), although he did not move to Coalbrookdale until 1709 (Cox 1990, 130). In 1710 Darby and partners obtained a lease from the Countess of Bridgewater to mine copper ore at Pymhill, near Clive, 10km north of Shrewsbury (Cox 1990, 130; Trinder 2000, 22). The brassworks appears to have been closed in 1714 but the copper smelting may have continued until the death of Abraham Darby in 1717. Documentary evidence (Belford 2007) suggests that these copper- and brassworks were sited in the vicinity of the Lower Furnace (approximately 400m to the north of the excavations at Upper Forge). There are no later documentary references to the smelting of copper in Coalbrookdale and so it is likely that some or all of the copper working debris recovered from the excavations at the Upper Forge relate to the activities of Abraham Darby in 1706–1717.

COPPER WORKING MATERIALS EXAMINED



Figure 1. Sample 3, copper ore



Figure 2. Sample 4, copper slag

The excavations at Upper Forge recovered three categories of material that are related to the smelting of copper and/or manufacture of brass: copper ore (Figure 1), copper slag (Figure 2) and crucibles. Single samples of ore (sample 3 from context [12311]) and slag (sample 4, from context [12206]) and two crucibles (samples 8 and 9, both from context [12179]) were selected for detailed examination (other sample numbers relate to steel cementation furnace material and are reported on in Belford and Ross 2007).

METHODS

All samples were examined visually before being prepared for scientific examination and analysis. Fragments of each sample were selected for microscopic examination and analysis and detached using a rock saw. These fragments were vacuum impregnated with epoxy resin and ground and polished to a 1-micron finish.

The polished specimens were examined using a reflected light microscope and a scanning electron microscope (FEI Inspect F). Chemical compositions of regions, droplets and distinct crystalline phases were determined using an energy dispersive spectrometer (Oxford Instruments INCA X-act) attached to the scanning electron microscope. The combined use of both techniques is referred to below as SEM-EDS.

Further fragments from each sample were prepared for analysis with an X-ray diffractometer (Bruker D8) to determine the mineral phases present. These samples were crushed (particle size <0.1mm) using a hardened steel shot mill. The XRD spectra were compared with the JCPDS Power Diffraction File database. In addition a fragment of sample 3 (copper ore) was prepared as a polished thin section and examined using a polarised transmitted and reflected light petrological microscope.

SAMPLE 3

Thin section

The thin section of this sample showed that it is a medium-grained sandstone (quartz arenite). Most grains are subrounded to subangular and show a restricted size range. Compositionally the rock is very mature dominated by monocrystalline and polycrystalline quartz grains accompanied by lesser amounts of alkali feldspar and rock fragments. There is no clay fraction, and heavy minerals, plagioclase and mafic minerals are rare to absent and neither the feldspars nor quartz show significant syngenetic overgrowths. Monocrystalline quartz grains showing uniform or strained extinction are approximately equal in amounts to polycrystalline quartz grains that include stretched quartz, quartzite,

rarer sandstones and pale-coloured to brown fine-grained chert/jasper. A little pressure solution can be seen where adjacent quartz grains touch.

Potassium feldspar grains including very rare microcline are tabular to subrounded and show slight alteration along their cleavage planes; some of this alteration is to chrysocolla. Very locally potassium feldspar overgrowths invade void spaces. Very rare, polysynthetically twinned plagioclase and compacted phyllosilicate are present.

Locally, coarse-grained, twinned baryte directly cements clastic grains but elsewhere baryte is separated from the clasts by thin chrysocolla rims that appear to be replacing the sulphate.

Chrysocolla is the main cement and directly cements clasts and/or infills voids between them. Two main generations of chrysocolla are present; the earlier is very fine-grained chrysocolla and the later botryoidal chrysocolla forms rims about voids enclosing baryte. This later chrysocolla varies from green to brown in plane polarised light. Trace amounts of 10–40µm diameter acicular malachite occur within the chrysocolla.

A range of other minerals were also observed but these are mostly very rare.

The sample is a pure sandstone showing two generations of copper mineralisation. An earlier baryte-minor copper sulphide episode is present cementing clastic grains, and there is a later chrysocolla–minor malachite episode that at least locally replaces the earlier mineralisation. The mineralisation is typical of that found in the Permo-Triassic rocks of central Britain. However, in detail it is unlike material from Alderley Edge in missing any lead or zinc phases.

XRD

The XRD analysis revealed the presence of quartz (SiO_2), barytes (BaSO_4) and orthoclase (an potassium feldspar, KAlSi_3O_8). The XRD analysis was unable to provide confirmation of the presence of chrysocolla. Typically this phase is poorly crystalline and so difficult to detect by this method.

SEM-EDS

The examination of the ore sample with the scanning electron microscope confirmed many of the observations made above based on the examination of a thin section of the ore. The SEM-EDS analysis confirms that the sample is composed of grains of silica and occasional orthoclase crystals with a copper-bearing matrix (Figure 3; Table 1). The copper bearing matrix contains copper, silicon and oxygen in proportions which correspond fairly closely to chrysocolla ($\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}$).

Table 1. Chemical composition of sample 3. Bulk represents the average of 20 separate areas. All results normalised to 100wt% except for 'chrysocolla'

	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	SO ₃	K ₂ O	CaO	TiO ₂	FeO	CuO	ZnO	BaO
bulk	<0.1	0.1	1.8	82.9	1.0	0.8	0.4	0.1	0.1	11.0	0.2	1.6
silica	<0.1	<0.1	0.1	99.9	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
feldspar	1.1	<0.1	19.0	64.0	<0.1	15.0	0.1	<0.1	<0.1	0.2	<0.1	0.6
barytes	<0.1	<0.1	<0.1	0.6	33.0	<0.1	<0.1	0.1	<0.1	0.2	<0.1	63.9
'chrysocolla'	<0.1	0.1	1.6	41.9	0.4	<0.1	1.3	<0.1	0.2	40.2	0.3	<0.1

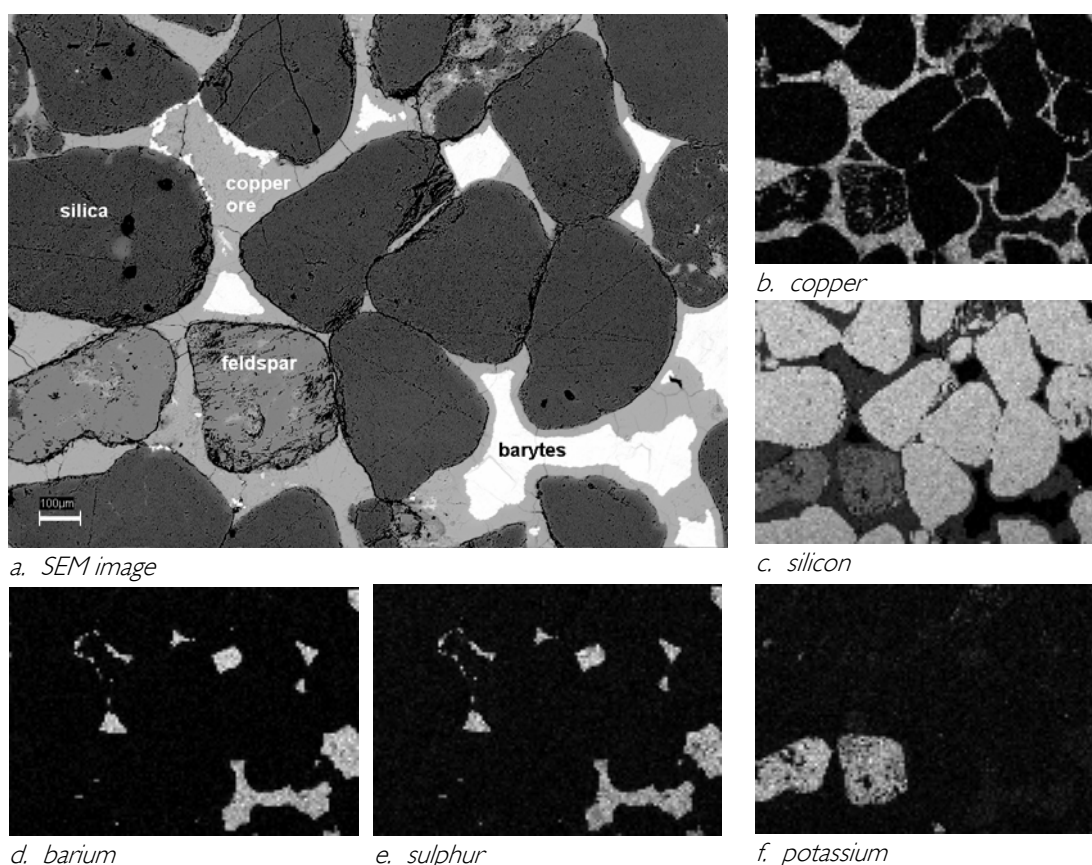


Figure 3. SEM image of sample 3 (brightness proportional to average atomic number) and elemental X-ray maps showing the distribution of five main elements (whiter areas indicate higher concentrations of the individual elements)

The most likely source for this ore would appear to be the copper ore deposits just north of Shrewsbury which are known to have been exploited by Abraham Darby and partners in the early 18th century.

SAMPLE 4

XRD

The XRD analysis revealed the presence of fayalite (Fe_2SiO_4), magnetite (Fe_3O_4), hedenbergite ($(\text{Ca,Fe})\text{SiO}_3$) and a barium aluminium silicate ($(\text{Ba,Al})\text{SiO}_3$).

SEM-EDS

The examination of the slag sample confirmed the presence of the mineral phases identified by XRD and also showed the presence of matte (copper-iron sulphide). Table 2 provides a bulk chemical composition of the slag avoiding any trapped matte particles as well as the composition of other phases determined using the SEM in spot mode. Table 3 provides the average matte composition by analysing several matte inclusions. Both fayalite and magnetite (Figure 4) were present as large enough crystals to allow complete confidence in their analysis in spot mode. The hedenbergite and the barium aluminium silicate, however, were mostly present as small crystals up to 10 microns across (Figure 5) so the chemical analyses of these phases may include some material from surrounding phases.

Table 2. Chemical composition of slag (bulk represents the composition of the slag without the matte). All results normalised to 100wt%.

	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	TiO ₂	MnO	FeO	CuO	ZnO	BaO
bulk	0.3	0.4	3.9	30.3	0.9	1.4	0.7	7.0	0.2	0.7	48.6	<0.1	0.6	5.1
fayalite	0.1	1.2	0.1	28.8	0.2	<0.1	<0.1	2.0	<0.1	1.2	65.5	<0.1	0.4	0.2
hedenbergite	0.4	<0.1	2.5	39.4	2.1	2.1	0.2	19.9	0.6	0.3	29.4	0.3	0.6	2.3
BaAl ₂ Si ₃ O ₁₀ ?	0.1	<0.1	19.6	38.4	0.4	0.5	3.5	2.4	0.2	<0.1	7.2	<0.1	0.2	27.2
magnetite	<0.1	<0.1	3.5	1.5	<0.1	<0.1	<0.1	0.3	2.4	0.4	91.2	<0.1	0.4	<0.2

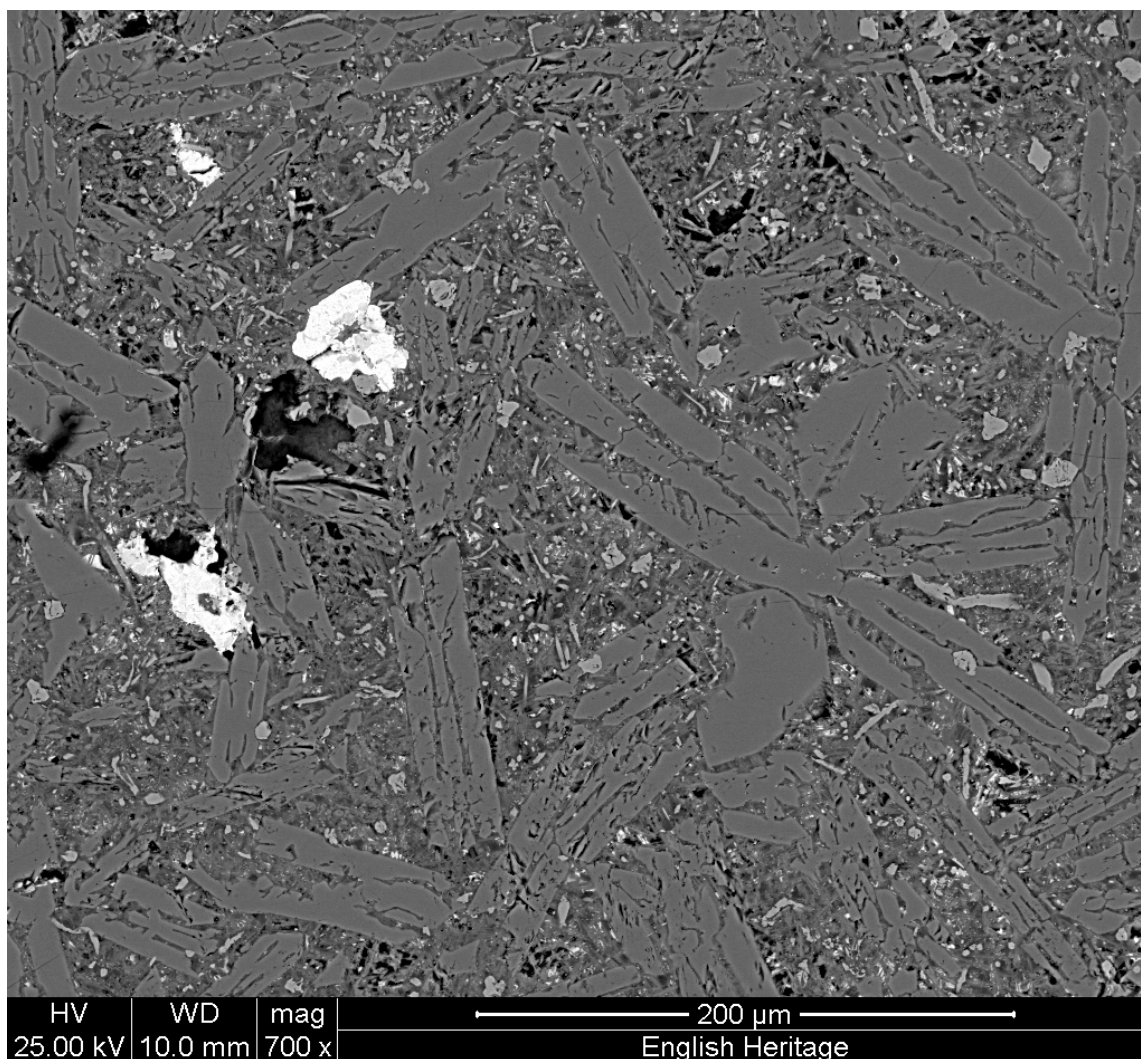


Figure 4. SEM image of sample 4 (copper slag). The bright droplets are matte, the occasional small light grey crystals are magnetite and the large medium grey laths are fayalite. The matrix between the fayalite laths is composed of several phases (see Figure 5).

Table 3. Average chemical composition of matte inclusions in the slag.

S	Fe	Cu	Zn	Ag
27.0	23.8	48.4	0.8	<0.2

The microstructure of this slag is markedly different to the mid 18th-century copper smelting slag from Warmley (White and Dungworth 2007). The Warmley slag, which was glassy with unreacted silica and large matte inclusions, was interpreted as ore furnace slag, which is slag from the first stage of copper smelting. The lower silica and higher iron oxide content of the Coalbrookdale slag, as well as the small size of the matte inclusions,

suggests that this slag was formed during one of the later stages of copper smelting. There is insufficient comparative material available to allow a positive identification of the exact process which produced this slag.

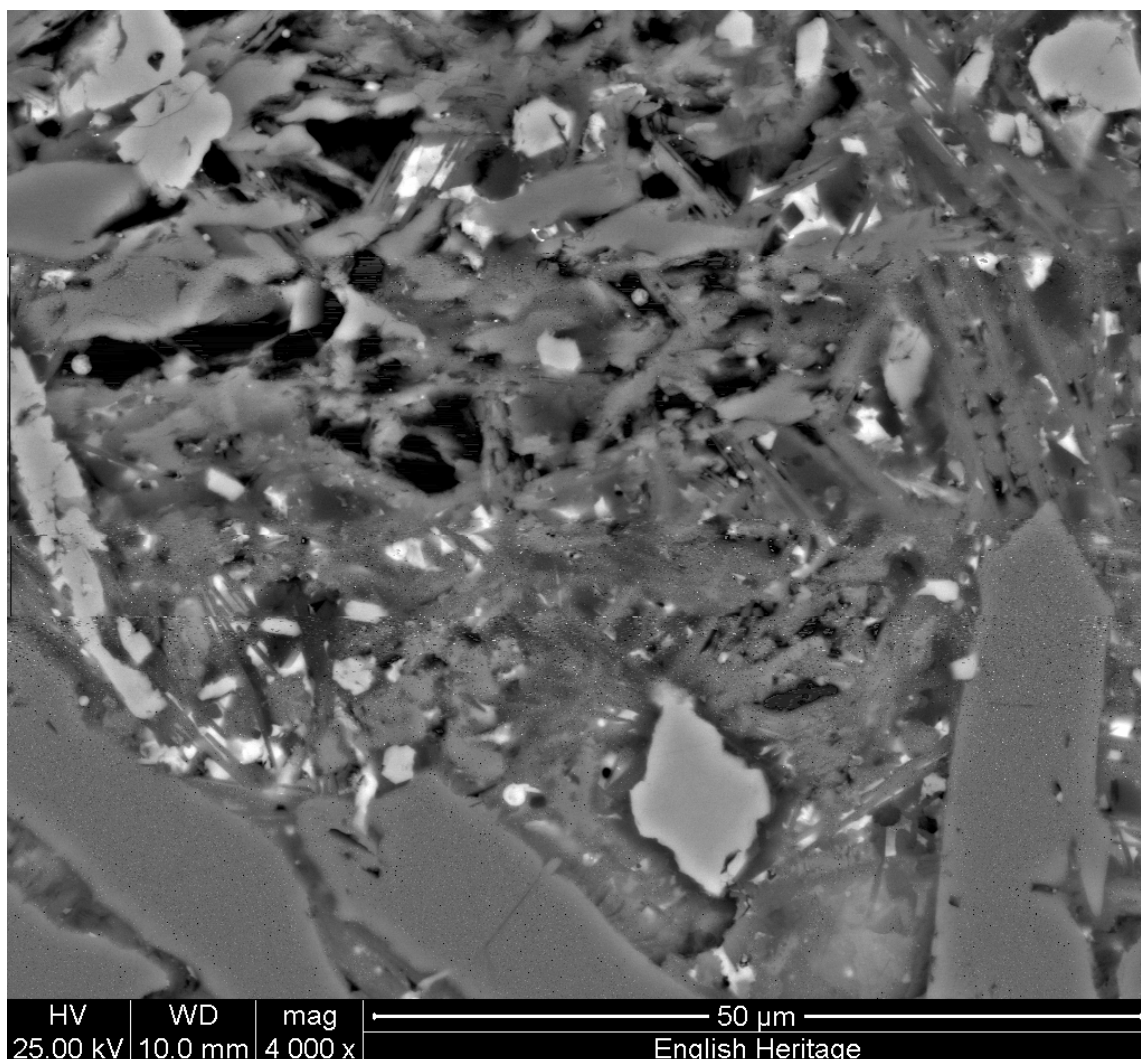


Figure 5. SEM image of sample 4 (copper slag) showing the complex multiphase matrix which contains hedenbirgite and a barium aluminium silicate as well as some magnetite and fayalite

SAMPLE 8

XRD

Two sub-samples from sample 8 were selected for analysis by XRD: sample 8a from the body of the crucible and sample 8b from the interior vitrified surface of the crucible.

The XRD analysis of sample 8a showed the presence of quartz (SiO_2), tridymite (SiO_2), cristobalite (SiO_2), gahnite (ZnAl_2O_4), mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and rutile (TiO_2). Quartz, tridymite and cristobalite are all forms of silica: quartz is the stable form of silica below 870°C , tridymite is the stable form between 870 and 1470°C , and cristobalite is the stable form above 1470°C (Deer *et al.* 1966, 341). The use of silica polymorphs as indicators of the temperatures to which refractory materials have been exposed is difficult as most will occur outside their stability fields. Moreover, the transformation of one form of silica into another is also influenced by the presence of other materials, especially alkalis (Eramo 2005) and so the presence of cristobalite does not prove that the crucible was exposed to 1470°C . The presence of mullite and tridymite suggests the high temperature ($>1200^\circ\text{C}$) breakdown of kaolinite (Eramo 2005; Martín-Torres *et al.* 2006; 2008).

The XRD analysis of sample 8b (the interior vitrified surface of the crucible) showed the presence of augite ($\text{CaMgSi}_2\text{O}_6$), a zinc aluminium iron spinel ($\text{ZnAl}_{1.9}\text{Fe}_{0.1}\text{O}_4$), covellite (CuS), hyalophane (a barium-rich potassium feldspar, $\text{K}_{0.6}\text{Ba}_{0.4}\text{Al}_{1.42}\text{Si}_{2.58}\text{O}_8$), anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), tridymite (SiO_2), quartz (SiO_2), and sanidine ($[\text{K,Na}][\text{Si,Al}]_4\text{O}_8$).

SEM-EDS

The SEM-EDS examination and analysis of crucible sample 8, in particular the interior vitrified surface (sample 8b), proved to be challenging as the crucible had clearly undergone a degree of corrosion after deposition. The ceramic fabric of the crucible (8a) is rich in silica and alumina and would be highly refractory. The presence of zinc and copper oxides in the fabric of the crucible probably reflects the use of the crucible for working copper-zinc alloys. The concentration of zinc found in the fabric of the crucible is high and reflects the presence within the crucible fabric of abundant small crystals of zinc-aluminium-iron spinels (Figure 6). Zinc-rich spinels have also been noted in two early 17th-century crucibles from Taynton, Gloucestershire which are interpreted as possible brass cementation vessels (Dungworth and Wilkes in preparation).

Table 4. Chemical composition of sample 8 (a = crucible fabric; b = interior vitrified surface). All results normalised to 100wt%

	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	TiO ₂	FeO	CuO	ZnO	BaO
a	1.6	0.3	19.3	62.9	<0.1	<0.1	0.7	0.2	1.1	1.7	0.4	11.8	<0.2
b	0.4	3.9	12.3	45.6	0.5	0.2	1.9	20.0	0.6	7.4	0.3	1.7	4.6

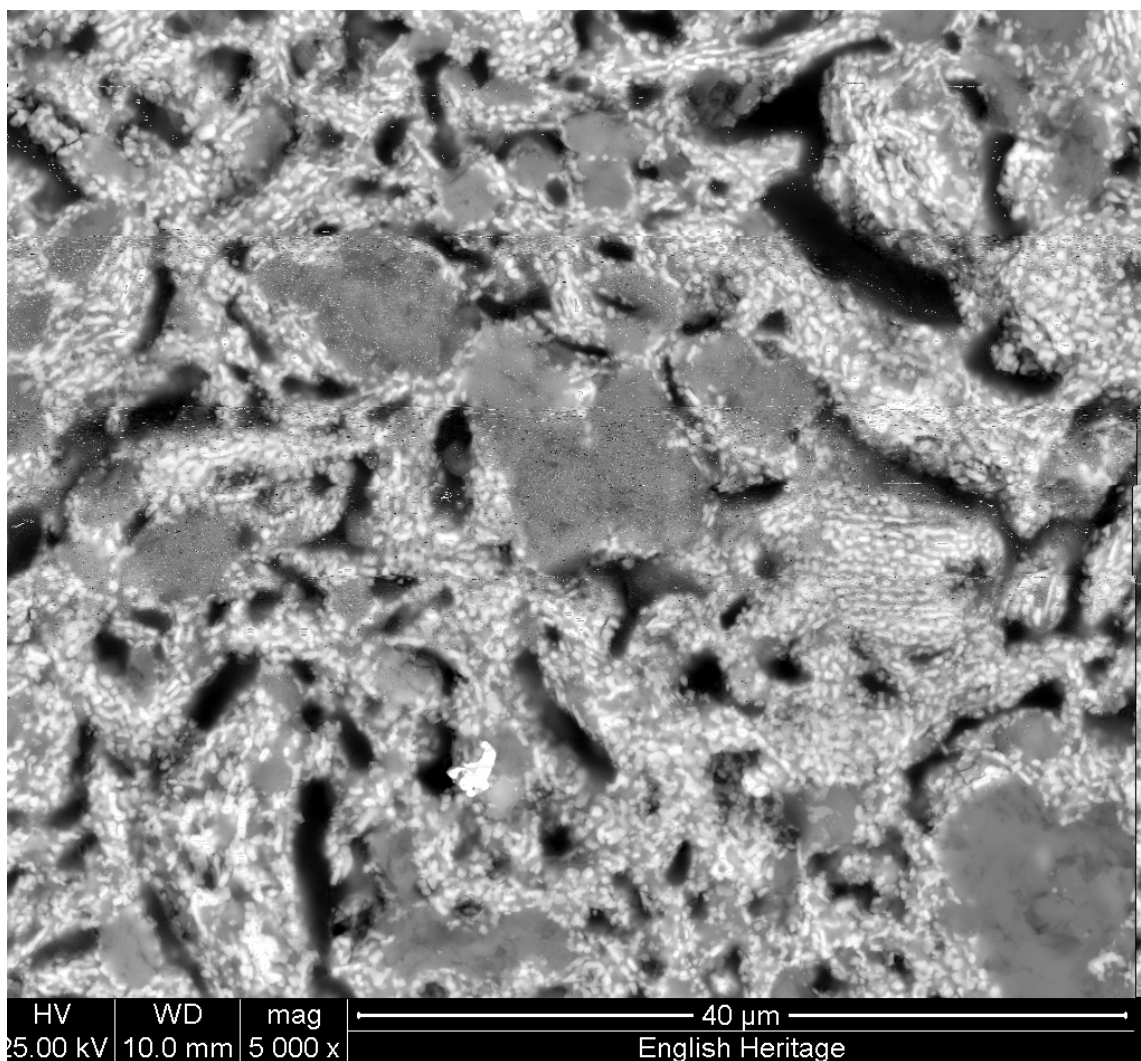


Figure 6. SEM image of the ceramic fabric of a crucible (sample 8a). The small bright crystals are zinc-aluminium spinels

The vitrified interior surface of this crucible contained a range of crystalline phases (as confirmed by the XRD analysis). Compared with the crucible fabric, the interior vitrified surface shows elevated levels of magnesium, calcium and barium (Table 4). It is possible to suggest that magnesium and calcium might simply derive from wood ash, the elevated levels of barium are less easily explained. One possible source of barium is the barytes present as a gangue mineral in many non-ferrous ores (in particular both copper and zinc ores). Dolomite and baryte are common gangue minerals associated with Mendip smithsonite (a zinc ore). A barium-enriched interior surface was also observed on one of the two brass-making crucibles from Taynton (Dungworth and Wilkes in preparation). It is not immediately obvious why the interior vitrified surface contains lower concentrations of zinc than the crucible fabric (it is assumed that the zinc derives from the material

charged into the crucible), however, the same phenomenon was seen with the Taynton crucibles.

Most of the copper alloy droplets within this crucible (both the ceramic fabric of the crucible and the interior vitrified surface) are rich in copper with relatively low concentrations of alloying elements (Table 5). Nevertheless, a wide range of minor elements is present and iron in particular is present at relatively high concentrations (1.2–2.3wt%). It is far from clear whether the copper alloy droplets trapped in this crucible truly reflect the composition of either a raw material charged into the crucible or a finished product. It is quite possible that this crucible was used over a long period of time to melt a range of different alloys and probably to manufacture cementation brass.

Table 5. Chemical composition of droplets (metallic and metal sulphides) within sample 8. All results normalised to 100wt%

	S	Fe	Ni	Cu	Zn	As	Ag	Sn	Sb	Pb
1	<0.1	1.6	0.2	91.0	6.4	0.2	<0.2	0.3	<0.2	<0.2
2	0.1	2.0	<0.1	95.7	0.8	0.7	<0.2	0.5	<0.2	<0.2
3	24.4	11.3	<0.1	63.4	<0.1	<0.2	<0.2	<0.2	<0.2	<1.0
4	<0.1	1.8	<0.1	93.6	1.0	1.3	0.2	1.3	0.2	0.6
5	<0.1	1.8	<0.1	93.4	0.8	1.6	<0.2	1.5	0.5	<0.2
6	<0.1	1.2	0.1	96.7	0.7	0.4	<0.2	0.4	<0.2	<0.2
7	<0.1	1.6	0.1	96.1	0.8	0.5	<0.2	0.5	<0.2	<0.2
8	<0.1	2.1	0.1	94.1	0.5	1.0	<0.2	1.5	0.3	<0.2
9	<0.1	2.3	0.1	93.4	1.6	0.6	<0.2	1.4	0.3	<0.2
10	25.9	12.0	<0.1	61.6	<0.1	0.1	0.4	<0.2	<0.2	<1.0
11	25.6	12.1	<0.1	61.6	<0.1	<0.1	0.6	<0.2	<0.2	<1.0

Three of the analysed droplets are not metallic but are copper-iron sulphides. While copper-iron sulphides (matte) were encountered in sample 4, where they are interpreted as indicators of the type of metallurgical process that was undertaken, they are also known to occur on the surface of corroded copper-based artefacts (eg Duncan and Ganiaris 1987; Tweddle 1992, 908) especially where these artefacts have been buried in anaerobic environments. This crucible was recovered from a well [12179] which would have provided a burial environment suitable for the formation of copper-iron sulphide corrosion products. The only possible reason why the presence of sulphides in this crucible might not be immediately dismissed as corrosion products is the presence of small concentrations of silver in these droplets (Table 3). It is possible that a silver-rich grade of matte was treated in this crucible to extract the silver that it contained.

SAMPLE 9

XRD

Two sub-samples from sample 9 were selected for analysis by XRD: sample 9a from the body of the crucible and sample 9b from the interior vitrified surface of the crucible. The XRD analysis of sample 9a showed the presence of quartz (SiO_2), tridymite (SiO_2), cristobalite (SiO_2), a zinc aluminium iron oxide ($\text{ZnAl}_{1.9}\text{Fe}_{0.1}\text{O}_4$), mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and rutile (TiO_2). The XRD analysis of sample 9b showed the presence of quartz (SiO_2), hyalophane (a barium-rich potassium feldspar, $\text{K}_{0.6}\text{Ba}_{0.4}\text{Al}_{1.42}\text{Si}_{2.58}\text{O}_8$) and a zinc aluminium iron oxide ($\text{ZnAl}_{1.9}\text{Fe}_{0.1}\text{O}_4$).

SEM-EDS

The SEM-EDS examination and analysis of this crucible (sample 9) showed many similarities with sample 8. The ceramic fabric of both crucibles is almost identical and they share the same chemical composition (especially if the zinc content is discounted, cf Tables 4 and 6).

Table 6. Chemical composition of sample 9 (a = crucible fabric; b = interior vitrified surface; c = exterior vitrified surface). All results normalised to 100wt%

	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	TiO ₂	MnO	FeO	CuO	ZnO	BaO
a	0.6	0.3	21.0	69.0	<0.1	<0.1	0.6	0.2	1.2	<0.1	1.6	<0.1	5.5	<0.2
b	1.1	1.4	11.0	49.5	0.3	0.2	3.7	9.7	0.5	1.1	4.7	<0.1	7.8	9.0
c	0.7	0.9	24.5	50.9	0.2	<0.1	1.0	6.4	0.8	0.2	9.3	<0.1	3.5	1.6

Table 7. Chemical composition of metal droplets within sample 9. All results normalised to 100wt%

	S	Fe	Ni	Cu	Zn	As	Ag	Sn	Sb	Pb
1	<0.1	0.6	<0.1	85.2	12.8	0.9	<0.2	<0.2	<0.2	0.5
2	<0.1	0.6	0.1	82.6	15.7	0.3	0.2	<0.2	0.3	<0.2
3	<0.1	0.5	0.2	81.0	16.4	0.2	0.3	0.2	0.7	0.6
4	<0.1	0.6	0.2	75.3	23.6	<0.2	<0.2	<0.2	0.4	<0.2
5	<0.1	0.6	0.2	74.4	23.8	0.2	<0.2	<0.2	0.4	<0.2
6	<0.1	1.0	0.2	94.3	2.8	1.4	<0.2	<0.2	0.3	<0.2
7	<0.1	0.5	0.2	94.5	0.7	2.3	0.7	<0.2	1.1	<0.2
8	<0.1	0.5	<0.1	84.9	11.1	0.7	0.2	<0.2	<0.2	2.2
9	0.5	0.2	0.1	95.4	0.9	2.1	0.3	<0.2	<0.2	0.3
10	<0.1	0.1	<0.1	95.7	2.8	0.6	<0.2	<0.2	<0.2	0.9
11	<0.1	0.1	<0.1	96.6	0.3	2.7	<0.2	<0.2	<0.2	<0.2
12	<0.1	0.1	<0.1	97.8	1.7	<0.2	<0.2	<0.2	<0.2	<0.2

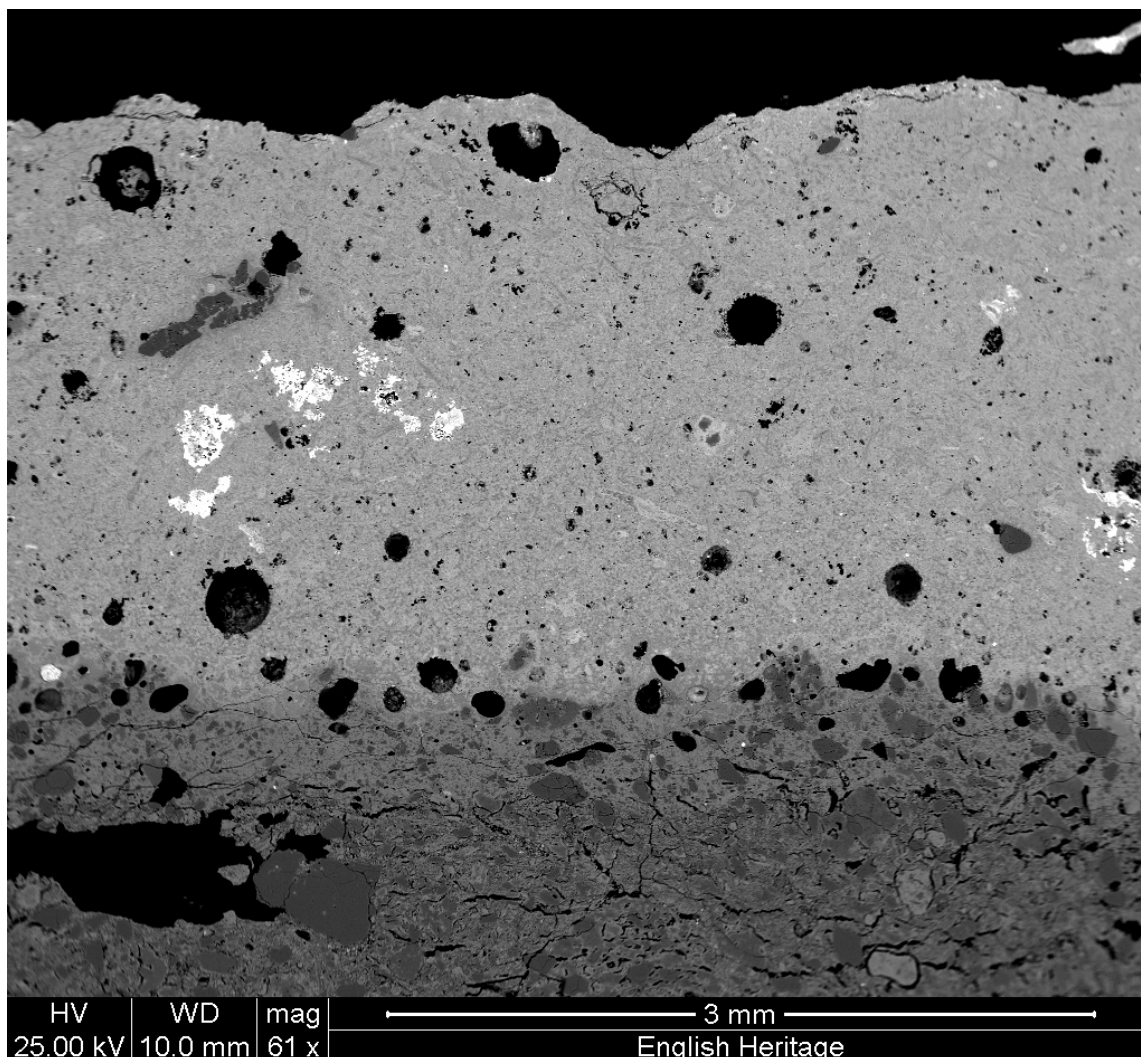


Figure 7. SEM image of the interior vitrified surface of crucible 9. The white regions in the light grey vitrified surface are copper alloy droplets.

The interior vitrified surface of this crucible (Table 7, 9b; Figure 7) contains a range of crystalline phases (as confirmed by the above XRD analysis). Like the crucible described above (sample 8) the interior vitrified surface of this crucible shows elevated levels of elements which might indicate the presence of barytes as a gangue mineral. The metallic droplets trapped in the interior vitrified surface of this crucible (Figure 7) show a wide range of chemical compositions (Table 8). Zinc concentration varies from less than 1wt% to almost 25wt%, but the tin and lead contents are very low. Several minor elements, such as arsenic and antimony were also detected. No copper-iron sulphide droplets were detected in sample 9.

Sample 9 has an exterior vitrified surface (Table 7, 9c) which shows elevated levels of iron and aluminium with only modest increases in the potassium and calcium. The chemical characteristics of this surface suggest that it formed as the result of reactions between the

crucible fabric and coal ash rather than wood ash. This indicates that the crucible was heated in a coal-fired furnace.

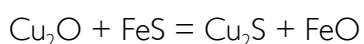
DISCUSSION

What is the relationship between the copper ore (sample 3) and the copper slag (sample 4)?

The sample of copper ore (sample 3) has a suite of minerals and a texture which suggests that it derives from the Permo-Triassic rocks of central Britain. There are, however, sufficient differences between this sample and any of the examined specimens from Alderley Edge to rule out that site as the source of the ore. The most likely source for this ore would appear to be the copper ore deposits just north of Shrewsbury which are known to have been exploited by Abraham Darby and partners in the early 18th century.

The sample of slag (sample 4) contains small droplets of copper matte and is clearly a copper smelting slag. The relatively high iron content and absence of free-silica suggests that this slag was not the by-product of the first stage of smelting. Lack of comparative studies, however, makes it difficult to identify which of the many later smelting stages produced this slag.

Some aspects of the copper smelting slag show close parallels with the ore which allow the linking of the two — it is likely that the slag was a by-product of smelting the copper ore examined (sample 3). Both ore and slag are free from lead and contain low levels of zinc, and both contain significant concentrations of barium. Nevertheless there are aspects of the copper slag which suggest that the copper ore from north of Shrewsbury was mixed with at least one other ore. Sample 3 contains the non-sulphide copper mineral chrysocolla ($\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}$) whereas the slag contains matte (copper-iron sulphides) which is produced when smelting sulphide ores. It is therefore likely that the non-sulphide ore from north of Shrewsbury was blended with a sulphide ore, to improve the efficiency of the smelting process, which appears to have been an important part of the Welsh Process of copper smelting (Tylecote 1992, 149). The Welsh Process is usually described as comprising a series of roasting steps to convert iron sulphides into iron oxides, and melting steps in which the iron oxide was separated into a slag. The Welsh Process made use of reverberatory furnaces for both roasting and melting, although such furnaces were first applied to the smelting of copper in the 1680s (Jenkins 1933–34). The Welsh process relied on a double decomposition reaction between non-sulphide ores and the iron sulphide in pyritic (sulphide) ores,

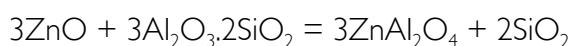


The oxidised ore could be obtained from suitable naturally-occurring ores or from roasted pyritic ores.

There is insufficient information to determine at what stage double decomposition became an important part of reverberatory copper smelting, however, the samples investigated here show that it was in use in Coalbrookdale between 1706 and 1717. It is quite possible that double decomposition formed part of the reverberatory furnace copper smelting technology that was developed in the 1680s (Jenkins 1943–45). There is also the possibility that double decomposition through the application of mixed ore charges contributed to smelting at an even earlier date. In 1585, Ulrich Frosse (a German copper smelter in South Wales) wrote requesting ‘when you do send any more ore, if you can, send of all sorts. The better it will melt and with more profit’ (Donald 1955, 344).

What were the crucibles (samples 8 and 9) used for?

The two crucible examined exhibit some characteristics which indicate that they may have been used as brass cementation crucibles. In both cases the ceramic fabric of the crucibles contains high concentrations of zinc which have led to the formation of zinc-aluminium spinels (gahnite, often with some substitution by iron). A study by Vorob'eva *et al* (1971) showed that gahnite tends to form in alumina-silica retorts used in zinc distillation. Initial firing of the retorts led to the formation of mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). During use zinc oxide vapour would penetrate the ceramic retorts and react with the mullite to give gahnite and silica (at temperatures as low as 950°C),



(the mullite would have formed during the initial firing of the retorts).

While zinc enrichment in a crucible fabric may simply be caused by melting a copper-based alloy which contains zinc (Dungworth 2001; Nicholas 2003), the composition of the inner vitrified layers indicates that these crucibles were probably used for the production of brass from zinc ore. The interior vitrified surfaces of both crucibles contain elevated concentrations of a number of oxides (compared to the crucible fabric). The most striking of these is barium, which was not detected in the ceramic fabric of the crucible and is rarely detected in the interior vitrified surfaces of crucibles used to melt copper alloys. Barium is often found as an accessory mineral (barytes) in non-ferrous ores and this is the most likely source of the barium in these crucibles. Zinc ores are often associated with a range of accessory minerals, including barytes.

The copper alloy droplets trapped in these crucibles show negligible tin and lead contents and variable copper and zinc contents. The samples with the lowest zinc contents

(<1wt%) may represent the copper charged into the crucible for the cementation process. Those with greater zinc contents (up to 24wt%) may approximate to the composition of the brass that was manufactured. Nevertheless, the location of these droplets within these crucibles is likely to mean that they were exposed to varying conditions over time, some of which would have increased their zinc content (cementation) and some of which would have reduced their zinc content (melting of the brass or later re-use of the crucibles).

Crucible 8 also contains occasional copper-iron sulphide droplets. While it is possible that these simply represent the corrosion of the copper alloy droplets in an anaerobic burial environment, it is also possible that the sulphide droplets represent matte which was deliberately melted in this crucible. The presence of small amounts of silver in the matte droplets increases the likelihood that these copper-iron sulphide droplets are matte and not simply corrosion.

CONCLUSION

The examination of industrial samples from the excavations of the site of the 17th-century steel cementation furnaces at Upper Forge, Coalbrookdale have provided evidence for the production of copper and brass. The ore would appear to derive from the mines worked by Abraham Darby and partners north of Shrewsbury in the early 18th century. The slag is clearly the result of smelting copper ores, including the ore from north of Shrewsbury, but contains matte (copper-iron sulphides) which shows that the slag was the result of smelting a charge that contained at least some sulphide ores. Later accounts of copper smelting stress the importance of combining oxidised ores with sulphide ores as the two would react together to increase the copper content of the resulting matte. No samples of the sulphide ore were recovered during the excavations at Coalbrookdale although sulphide ores are not as brightly coloured as oxidised ores and so are more easily missed.

The two crucibles examined were used for the production of brass using the cementation process. It is possible that one of the crucibles was also re-used to melt a silver-rich grade of copper matte.

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