Analysis of Slag and Related Materials from the Beaconsfield A355 Eastern Relief Road: Areas B and C (BERR18; AYBCM: 2017.35)

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Introduction

Excavations along the Beaconsfield A355 Eastern Relief Road: Areas B and C (BERR18 centred on NGR SU 9491 9099) by Oxford Archaeology exposed a series of ditches containing late Iron Age/early Roman pottery (50 BC-AD 50) suggesting domestic activity within a loosely enclosed landscape.

Methods

All of the material was washed, dried and sorted using largely visual criteria (cf Historic England 2015). The material was sorted into different categories based on colour and surface morphology (and occasionally on an assessment of density and/or magnetic response). The categories of material identified include the following:

Slag cake (SC)	These are plano-convex (or concave convex) and approximately circular in plan. Slag cakes are usually identified as smithing slags (McDonnell 1991; Serneels and Perret 2003), although larger examples are identified as smelting slags (furnace bottoms).
Non-diagnostic slag (ND)	Most ironworking slag assemblages include a significant proportion of slag which lacks a diagnostic surface morphology that would allow the identification of the process(es) which produced them. In many cases, this is simply because the lumps of slag are small fragments of a larger whole; however, in some cases the lumps of slag are essentially complete but amorphous (Historic England 2015, Figure 18).
Crucible	Ceramic containers used to hold metal while it is being melted (Bayley and Rehren 2007).

The crucible was selected for scientific analysis. The aim was to provide information on the nature of the crucible (chemical composition and microstructure) as well as any vitrified surface and metal droplets. The crucible was cut using a rock saw and mounted in epoxy resin, and then ground and polished to a 1-micron finish. The microstructure of each sample was imaged using a back-scattered electron detector attached to a scanning electron microscope (SEM). In addition, the chemical composition of parts of the crucible was determined using an energy dispersive X-ray spectrometer (EDS) attached to the SEM.

Visual examination

Table 1. Summary recording of slag, etc from BERR18 (weight in grams)

Context	SC	ND	Crucible	Total
118	163	12.4		175.4
266			6.8	6.8
281	120			120
All	**283**	**12.4**	**6.8**	**302.2**

The visual examination of the industrial debris from BERR18 showed that there was just under 0.3kg of ironworking slag and a single (6.8g) crucible fragment (Table 1). The ironworking slag includes a small amount of non-diagnostic ironworking slag (12.4g) and two slag cakes (283g). The slag cakes are small and can be confidently identified as deriving from smithing rather than smelting. This quantity of iron smithing debris could have been produced in just a few days. On this evidence it is likely that blacksmithing was no more than an occasional activity.

The crucible fragment (Figure 1) has a profile which is consistent with other Iron Age crucibles (Wainwright 1979). These are small, shallow vessels with three corners pulled out to form a triangular bowl. The fabric of this crucible is very sandy and has a buff colour, with darker grey fabric and some vitrification on the interior surface. It is likely that the crucible was placed at the base of a charcoal fire and heated from above. The vitrified surface of the crucible contains few patches stained green by copper corrosion products (indicating that the crucible was probably used to melt copper alloys).

Figure 1. Photograph of the crucible fragment from context [266]

A single crucible fragment shows that *some* melting of copper alloy took place but it is difficult to be certain what scale of activity this represents. Crucibles are routinely recovered from Iron Age settlements of all sizes but occasionally the evidence includes kilograms of crucibles and moulds (*eg* Foster 1995; Wainwright 1979). It is possible that bronze casting was a regular activity at most sites, but site formation processes only preserve such full evidence at a few sites. Nevertheless, a single crucible fragment might represent no more than a single day's casting.

SEM examination and analysis of the crucible

The examination of the crucible using a scanning electron microscope (SEM) revealed details of its microstructure (Figures 2–5). The crucible is mostly made of quartz-rich clay (Figures 2 and 3) with a vitrified inner surface (Figures 4 and 5). The crucible fabric comprises abundant quartz grains (mostly 0.15–0.25mm, but with some examples much smaller) cemented together by a ceramic groundmass, but including numerous voids (cf Howard 1983). While naturally quartz-rich clay could be used as the raw material, such clays are not common. It is likely that at least some of the quartz inclusions represent deliberate temper to improve the heat-resistance (refractoriness) of the clay.

The quartz grains are euhedral and mostly rounded. While the shape probably reflects the geological weathering of quartz grains prior to the manufacture of the crucible, it could also be due to the high-temperature erosion of quartz when the crucible was in use. The quartz grains show highly variable degrees of cracking (cf Figures 2and 3). Cracking in quartz grains is usually the result of thermal stresses, and it is likely that the heating of the crucible was not uniform.

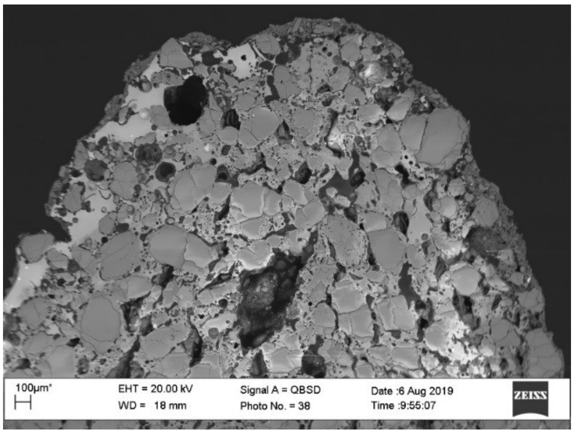

Figure 2. SEM image of the crucible showing the lip with the interior (vitrified) surface to the left and the exterior surface to the right. The ceramic fabric is dominated by quart grains displaying relatively little thermal cracking

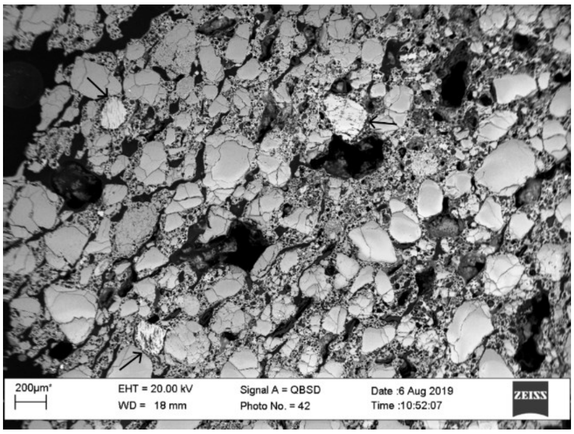

Figure 3. SEM image of the crucible showing the quartz-rich fabric. The quartz grains here show much more thermal cracking. A few other (non-quartz) inclusions are also present (indicated with black arrows)

The quartz grains are cemented together by a clay groundmass which has a varied texture. In some areas the groundmass contains numerous very small, irregular, and angular voids which suggests limited exposure to high temperatures. Other areas of groundmass show some vitrification and the formation of fewer, but larger voids, which tend to be rounded. Such vitrification is typical of temperatures required to melt copper alloys (1000–1200°C). Areas with no signs of vitrification are unlikely to have been exposed to temperatures above 800°C.

While quartz is the most abundant inclusion in the crucible fabric, other minerals are present (Figure 3). SEM-EDS analysis confirmed that these are potassium-rich feldspars. These are common minerals in clays and are unlikely to represent deliberate temper. Potassium feldspars decompose at high temperatures (1150°C, to form leucite and quartz) and their survival in the BERR crucible suggests that at least some regions were not exposed to high temperatures. The ceramic also shows moderately abundant voids and porosity. The voids are mostly highly irregular in shape and, as such, reflect the processing and forming of the clay. Such voids may have helped to improve the thermal insulation of the crucible and (perhaps more importantly) could have helped reduce crack propagation.

The crucible has a pronounced vitrified layer on its interior surface (Figures 4 and 5); no vitrification was detected on the exterior surface of the crucible. The vitrified surface appears to be present in two more-or-less distinct layers (Figure 4). Layer 1 (closest to the ceramic) contains numerous relict quartz grains in a glassy matrix. Layer 1 contains some copper alloy droplets as well as a variety of metal oxides. Porosity is present in layer 1 but is less abundant compared to the underlying ceramic. Layer 2 appears very bright in SEM images (Figures 4 and 5) because it contains a high proportion of metal oxides (especially cassiterite, SnO_2, and cuprite, Cu_2O). In many areas, layer 2 appears to have undergone post-depositional corrosion and weathering (Figure 5, cf Figure 1).

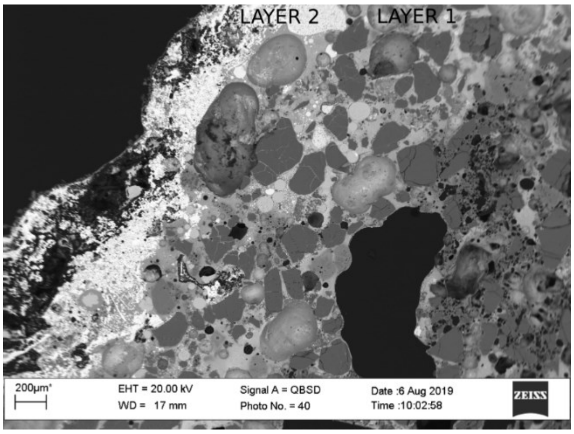

Figure 4. SEM image of the crucible showing the interior vitrified surface. This has two layers (annotated): layer 1 comprises abundant relict quartz in a vitrified matrix (with some copper alloy droplets), layer 2 is glassy but contains abundant metal oxide crystals (tin oxide and copper oxide)

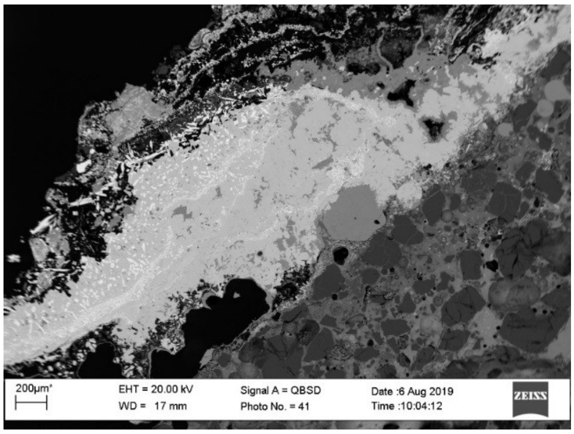

Figure 5. SEM image of the crucible showing the interior vitrified surface. This shows that the outermost portions of layer 2 have been subject to post-depositional weathering

The SEM-EDS analyses show that the crucible is silica-rich and that the vitrified layers contain elevated levels of copper and tin (Tables 2–5). The SEM-EDS analyses were directed to discrete areas (and occasionally discrete droplets or crystals). Layer 2 has suffered from some post-depositional weathering and so not all areas could be fully characterised.

Table 2. Chemical composition of areas of the crucible fabric (avoiding areas of surface vitrification). SEM-EDS data (weight %)

Area	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	FeO	Cu_2O	ZnO	As_2O_3	SnO_2	Sb_2O_3	PbO
1	<0.1	0.4	8.2	86.2	<0.2	1.1	0.1	0.22	<0.1	2.6	0.6	0.19	<0.2	<0.2	<0.2	<0.2
2	<0.1	0.5	9.9	84.8	<0.2	1.2	0.1	0.39	0.1	2.4	0.1	0.15	<0.2	<0.2	<0.2	<0.2
3	<0.1	0.3	9.7	84.8	<0.2	1.1	0.1	0.35	<0.1	2.8	0.2	<0.1	<0.2	<0.2	<0.2	<0.2
4	0.2	0.4	10.1	84.2	<0.2	1.7	0.1	0.40	<0.1	2.6	0.1	<0.1	<0.2	<0.2	<0.2	<0.2
mean	**<0.1**	**0.4**	**9.5**	**85.0**	**<0.2**	**1.3**	**0.1**	**0.34**	**<0.1**	**2.6**	**0.2**	**0.1**	**<0.2**	**<0.2**	**<0.2**	**<0.2**

The crucible contains high levels of silica (SiO_2) which would have tended to provide refractory (heat-resistant) properties (Table 1). Howard's examination of prehistoric ceramic crucibles using optical petrology (Howard 1983) shows these to be rich in quartz inclusions and so a high silica content is to be expected (although there are few published chemical analyses available to compare with the BERR crucible). The limited data on later (Roman and medieval) crucibles (*eg* Dungworth and Starley 2009; Dungworth 2015) suggests that these contained less silica (60–70wt% SiO_2) and more aluminium oxide (20–30wt% Al_2O_3).

The chemical compositions of the vitrified layers (1 and 2, see Tables 3 and 3) reflect their appearance: layer 1 is silica-rich (reflecting the presence of relict quartz grains) but does contain some metal oxides (especially copper and tin), while layer 2 is tin- and/or copper-rich. The tin to copper ratio is very high in the two metallic droplets analysed (Table 5) and far exceeds that usually found in later prehistoric copper alloys (Dungworth 1996). It is not certain that the composition of these droplets accurately reflects the nature of the alloy cast in the crucible. Metal droplets trapped in vitreous layers of a crucible could be subject to several period of heating (with associated metal loss due to oxidation). This could, over time, change the composition of the droplets.

Table 3. Chemical composition of areas of the surface vitrification of the crucible (layer 1). SEM-EDS data (weight %)

Area	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	FeO	Cu_2O	ZnO	As_2O_3	SnO_2	Sb_2O_3	PbO
1	0.2	0.4	6.3	72.5	<0.2	1.7	0.6	0.24	<0.1	1.8	14.9	<0.1	<0.2	1.0	<0.2	<0.2
2	<0.1	0.2	5.1	65.8	<0.2	1.4	0.5	0.22	<0.1	0.9	19.3	0.25	<0.2	6.1	<0.2	<0.2
3	0.3	0.3	6.3	66.8	<0.2	1.4	0.3	0.27	<0.1	1.6	21.8	<0.1	<0.2	0.6	<0.2	<0.2
mean	**0.2**	**0.3**	**5.9**	**68.4**	**<0.2**	**1.5**	**0.5**	**0.24**	**<0.1**	**1.5**	**18.7**	**<0.1**	**<0.2**	**2.6**	**<0.2**	**<0.2**

Table 4. Chemical composition of areas of the surface vitrification of the crucible (layer 2). SEM-EDS data (weight %)

Area	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	FeO	Cu_2O	ZnO	As_2O_3	SnO_2	Sb_2O_3	PbO
1	<0.1	0.6	3.5	17.4	<0.2	0.3	0.6	0.25	<0.1	2.4	71.8	<0.1	<0.2	2.4	0.7	<0.2
2	<0.1	0.5	12.1	40.4	<0.2	2.3	1.6	0.19	<0.1	1.4	39.8	<0.1	<0.2	1.6	<0.2	<0.2
3	<0.1	0.5	9.5	46.8	0.2	2.6	2.4	0.63	<0.1	1.9	13.9	<0.1	<0.2	21.2	<0.2	<0.2
4	<0.1	1.4	3.6	24.6	0.3	0.8	8.8	<0.1	<0.1	0.4	8.4	<0.1	<0.2	49.8	1.5	0.4
mean	**<0.1**	**0.8**	**7.2**	**37.3**	**<0.2**	**1.5**	**3.3**	**0.27**	**<0.1**	**1.5**	**33.5**	**<0.1**	**<0.2**	**18.8**	**0.6**	**<0.2**

Table 5. Chemical composition of copper alloy droplets within the surface vitrification of the crucible. SEM-EDS data (weight %)

Droplet	Fe	Ni	Cu	Zn	As	Sn	Sb	Pb
1	<0.1	0.3	69.8	0.3	0.4	27.7	1.5	<0.1
2	0.3	<0.1	66.7	1.7	<0.2	29.2	2.2	<0.1
mean	**0.2**	**0.1**	**68.3**	**1.0**	**<0.2**	**28.4**	**1.9**	**<0.1**

Discussion

The visual examination of the industrial debris shows that iron smithing and copper alloy casting took place. The scientific examination of the crucible shows that it has a fabric/texture which matches most later prehistoric crucibles: 'the final and most prolific Iron Age crucible fabric consists of carefully selected sand bound with a small proportion of clay' (Howard 1983, 496). Such very quartz-rich tempered crucibles are rarely seen in Roman (Dungworth and Starley 2009) and later (Dungworth 2015) crucibles and are a particularly Iron Age technological approach. Quartz is extremely refractory but is susceptible to chemical erosion, especially from metal oxides. Even in the absence of metal oxides, the quartz would undergo some erosion from the vitrified clay groundmass. It is likely that very quartz-rich fabrics would also be quite weak, especially at high temperatures. Poor strength was mitigated to some extent by the form of the crucibles (fairly shallow bowls), and probably reflects the fact that only a small quantity of copper alloy needed to be melted at one time. It is likely that there was little need to move the crucible and its molten metal. If the crucible was heated in the same fire as the moulds, then the molten contents of the crucible could simply be tipped into an adjacent mould. One advantage of using a very quartz-rich temper would be that the refractory quality of the clay itself would be of lesser importance — almost any clay would be suitable, so long as sufficient sand was added.

While the *chaîne opératoire* for crucible manufacture was well suited to the overall copper alloy casting needs, the execution of copper melting appears to be rather irregular. The clay texture shows that not all of the crucible was subject to the same degree of heat, even though Iron Age crucibles are typically rather small. Some parts of the crucible have a clay groundmass which shows no signs of vitrification (temperatures below 800°C?) while other parts have a completely vitreous groundmass (temperatures of 1000–1200°C). Similarly, the proportion of quartz grains with thermal cracks varies from area to area (suggesting varied temperatures).

The texture and chemical composition of the vitrified layers suggests that layer 2 represents oxidised metallic residue from melting copper alloys under imperfect melting conditions (insufficiently reducing). It is likely that layer 1 incorporates some charcoal ash and some vitrified crucible fabric. Layer 1 represents the infiltration of the crucible fabric by some vitreous material from layer 2. Between them, layers 1 and 2 constitute almost a third of the thickness of the crucible wall. This degree of vitrification suggests prolonged and/or repeated heating (or possibly poor refractoriness). The vitrified layers contain significant proportions of non-ferrous metals, in particular copper and tin. The virtual absence of zinc is significant as this metal is particularly volatile and is often present at high levels even in those crucibles used to melt copper alloys containing even modest levels of zinc (Dungworth 1999; Kearns *et al* 2010). The near absence of zinc in the BERR crucible suggest that none of the copper alloys melted in it contained more than traces of zinc. This evidence is consistent with the melting of tin bronze (cf Dungworth 1996) but extrapolating the precise chemical composition of the bronze melted from the available data is impossible. It is not certain how many times the crucible was used, whether the same alloy was melted each time, or if each melting was as skilled (*ie* minimal loss of metal through oxidation).

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