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ANALYSIS OF 17TH CENTURY
DELFTWARE POTTERY SHERDS FROM
LONDON

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Summary

A large assemblage of pottery kiln waste material, derived from the nearby Pickleherring pottery kiln, was discovered in the 17th century back-fill of a large 15th century pond, between Tooley Street and the Thames. The waste material included broken fired clay vessels covered in a friable white coating. The friable coating was found to be an unfired glaze consisting of four original components: finely ground, glassy, predominantly lead frit; particles of lead-tin oxide (lead stannate); particles of quartz and probably some fine clay. Calcium carbonate had crystallised in the glaze during burial and the particles of glass frit had weathered by varying amounts. The clay fabric was inhomogeneous in some areas and was made up by mixing at least two clays together; one of which was rich in calcium oxide. The glaze and clay compositions are consistent with those of Delftware pottery, with its characteristic tin oxide opacified, lead glaze and mixed clay fabric, which was produced in London during the 17th and 18th centuries.

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Analysis of 17th Century Delftware Pottery Sherds from London.

Sarah Paynter

Introduction

Several sherds of pottery were supplied, all from site BFS 88, context 4. These sherds represent different parts of broken vessels including fragments of the bases and rims. All of the fragments consist of a fired clay substrate covered with a friable white coating. The clay in each case has fired to a pale pink / buff colour. The walls of the vessels are approximately 8mm thick.

These fragments were found during the course of the excavation of a site in London where Delftware was produced during the 17th and 18th centuries. Delftware is characterized by an opaque white glaze, sometimes with decoration, in a variety of different colours, applied over the glaze. It is known that, during the production process, vessels were first biscuit fired and then dipped in a glaze slop. There followed a glost firing to mature the glaze. Therefore the friable white coatings were anticipated to be unfired or partially fired tin-opacified lead glazes of the type used to produce Delftware. Analysis was undertaken to establish whether the friable coating was an unfired or partially fired lead-tin glaze.

Methodology

XRF analysis of a sherd was undertaken using a tube with a rhodium target run at 35keV and 100 μ A. This technique allows the determination of the elements present in a sample without the need for destructive sampling. The technique is more sensitive for heavier elements, therefore is particularly suitable for detecting lead and tin.

XRD analysis of a powdered sample of the friable coating was undertaken using a scan rate of 0.02 $^{\circ}2\theta/s$ between 10 and 70 degrees. This technique enables the identification of the different crystalline phases present in the sample, as each has a characteristic diffraction pattern from which the crystal structure can be determined.

Small samples were taken from two of the sherds. These were mounted in a cold-curing resin and polished to obtain a flat surface. The cross section of the sherds was then examined using a scanning electron microscope with attached energy dispersive X-ray analyser. This technique enables the fragments to be viewed at very high magnification. The characteristic X-rays emitted by the sample under the electron beam can also be analysed to determine the composition of different features of the sample.

Results

XRF analysis confirmed the presence of lead and tin in large quantities in the friable white coating, as well as iron and several other elements characteristic of the clay substrate.

XRD analysis showed the presence of cassiterite (tin oxide SnO_2), quartz (SiO_2), calcite (calcium carbonate CaCO_3) and lead silicates (for example Pb_2SiO_4 , $\text{Pb}_3\text{Si}_2\text{O}_7$ and /or Pb_3SiO_5). The peaks characteristic of these compounds obscured peaks from other compounds that might also be present. The presence of small amounts of lead-tin oxide (Pb_2SnO_4 and / or PbSnO_3), and lead oxide (PbO : litharge and / or massicot, or Pb_xO_y : another oxide of lead) is suspected.

In the SEM back-scattered electron images, figures 1 and 2, different compositions are shown by different shades of white through to black. A lighter shade indicates a feature that contains heavy elements such as lead or tin whereas a darker shade indicates an area that contains lighter elements such as silicon or aluminium. Thus the clay body appears a dark grey in the images and the areas in the glaze that appear white contain a lot of tin and lead.

SEM analysis revealed many interesting features. The first is that the glaze has not been fired at all. This can be deduced by the fact that the friable coating is clearly comprised of many very small, sharply-angled particles. If the glaze had been heated some fusing of these particles would be expected. There is a clear boundary between the clay substrate and the layer of glaze particles on the surface. Again, if the glaze had been heated we would anticipate some interaction between the glaze and the clay substrate.

The SEM images also illustrate the separation of the glaze particles, in terms of particle size, that has occurred when the glaze was applied (figure 1). The finer particles are nearer the clay substrate with the coarser particles towards the top. This separation would have occurred naturally because the glaze particles were applied in a suspension in water. This observation is supported by the fact that small craters and blisters can still be seen by eye in the glaze coating where bubbles popped as the glaze slop dried on the pot.

The glaze is made up of several distinct components:

1. Finely ground, angular glass frit (light and dark grey).
2. Particles of a crystalline lead-tin oxide complex (white).
3. Fine, crystalline calcium carbonate (light grey).
4. Rounded particles of quartz (dark grey).

(“Frit” here is used to mean the finely ground, largely glassy material produced when some of the glaze components are fired together then reground before being added to the glaze mixture.)

Some of the particles of glass frit are light grey and others dark grey. This indicates that the particles have different compositions. The lighter particles contain silica, and oxides of lead, calcium, potassium, sodium, magnesium and aluminium and a small amount of tin oxide. However during burial water has attacked many of these glass particles, leaching out nearly all of the elements from the glass and leaving just silica. These are the particles that appear dark grey. Some of the particles are at an intermediate stage. They have light grey cores surrounded by weathering layers, which appear as rings of differing shades of grey (figure 2).

The original glass frit would therefore have been produced by combining a small quantity of

the materials needed to produce an alkaline glass with a larger quantity of the materials needed to make a lead glass, plus a small amount of tin oxide.

The white particles are a mixture of lead and tin oxides with a small amount of silica. The particles are made up of crystals of the lead-tin oxide compound (PbSnO_3) that would have been made either by heating together lead and tin metals and skimming the combined oxide from the surface or possibly by heating together lead oxide and tin oxide in the presence of some silica, for example in a clay crucible.

Analysis of the unfired glaze layer as a whole shows that it contains large quantities of lead oxide, silica and tin oxide, as expected. However it also contains high levels of calcium carbonate and small quantities of phosphates. This level of calcium is unusually high for a glaze of this type and the form of the calcium carbonate, as very fine crystals amongst the glaze particles, indicates that this has crystallised on the sherds during burial. If calcium carbonate were being used as part of the glaze mixture, the potters would have fritted it with the other components as this compound takes a long time to completely dissolve and can otherwise lead to inhomogeneities in the glaze. It is also likely that the phosphates are the result of deposition from the ground water during burial.

The glaze layer also contains a small amount of aluminium oxide. Since neither the glass frit or lead-tin oxide particles contain a significant amount of aluminium oxide, this probably indicates that a small amount of fine clay was added to the glaze mixture along with these components. Glazes are usually made up of powdered components in a water suspension. However the powder often has a tendency to settle out, particularly if the glaze contains alkalis, such as sodium and potassium oxides. Adding a small amount of clay to the mixture will help keep the glaze components in suspension for longer.

The clay substrate itself is made up of different clays mixed together. In most cases the resulting fabric is fairly homogeneous but in one sherd there are areas with slightly different compositions. The most significant difference is the amount of calcium oxide present. It would appear that a calcium rich (calcareous) clay has been mixed with one, or several, others. The areas of clay that contain the most calcium have reacted to a greater extent and have become glassier when they were fired.

Conclusions

The glaze is unfired but has survived relatively well during burial. A gum or other additive may have been added to the glaze slop as a hardener, to prevent the glaze powder from brushing off the pot before it could be fired though no analysis has been undertaken that might identify the presence of organic materials of this type.

The glaze itself is made up of several components: a mixed alkali / lead glass frit (also containing a small amount of tin oxide); a small amount of clay; particles of lead-tin oxide plus some post-burial precipitates. The addition of a small amount of clay to the glaze would have helped to stop the glass particles from settling out of the glaze slop. This becomes a particular problem if alkalis are present in the glaze and it can make glaze mixtures very difficult to work with if not corrected.

The fabric of the pot is made up of a mixture of at least two different types of clay: the

principal difference between them being that one is calcareous and the others are not. Historical references (Britton, 1987) refer to locally available strong red clay and blue clay, both of which were “fat”, i.e. plastic, but shrunk a great deal as they dried. Uncorrected, this would cause the pots to warp and crack. So these clays were mixed with a third clay, which was white, weak and “short” i.e. not very plastic. The latter clay was not locally available and had to be purchased from elsewhere. It is likely that this white clay was the calcium rich clay detected in the analyses. As well as preventing warping and cracking of the pots as they dried, the addition of this clay would also have lightened the colour of the fired clay to a pale buff colour. This is far more suitable for the background to a white glaze than the strong red colour that would have been produced without the addition of the white clay. The regions of the mixed clay that contain greater concentrations of calcium have reacted to a greater extent than the calcium depleted regions, becoming more glassy and stronger.

The technology for producing tin-opacified lead glazes originated in the Islamic world beginning around the 8th to 9th centuries AD (Tite and Mason, 1997). It is interesting to note that Islamic potters also used pale-firing, calcium-rich clays to produce these wares. They also used tin oxide to opacify a wide range of glaze compositions: including lead glazes, mixed lead-alkali glazes and alkali glazes (Paynter, forthcoming; Tite et al, 1998). An ancient treatise (Allan, 1973) describes how potters would preheat lead and tin metals together, skimming the mixed oxides off the surface of the melt to use in their opaque glazes. Mixed lead-tin oxides, that could have been produced in this way, were found in the Delftware glazes.

There are several advantages to adding the tin oxide opacifier in combination with lead oxide.

1. It is more time and energy consuming to produce fine tin oxide particles by simply heating and grinding tin alone.
2. Tin oxide powder, if added alone, is more likely to settle out along the surface of the pot so that the final effect is more like a white background with a transparent glaze. If the tin oxide is added in the form of a mixed lead-tin oxide, it ensures that the tin oxide particles are spread uniformly throughout the glaze thickness to produce a homogeneous, opaque, white glaze.
3. If tin oxide is added alone, it is insoluble in the glaze. However if tin oxide is preheated with lead oxide, a particular lead stannate compound can form. This compound can dissolve in the glaze and then tin oxide crystallizes back out as many very small individual crystals. These small crystals are more efficient at scattering light than the larger particles that are the result of adding tin oxide alone (Molera et al, 1999).

In summary the glaze has been prepared according to a longstanding tradition originating in the Near East. However each step in the glaze preparation and clay preparation is necessary to the quality of the final product.

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Figure 1

An SEM back-scattered electron image showing the cross section of a sherd. The clay appears a dark grey colour at the top left of the image. The unfired glaze is the layer of particles at the bottom right of the image.

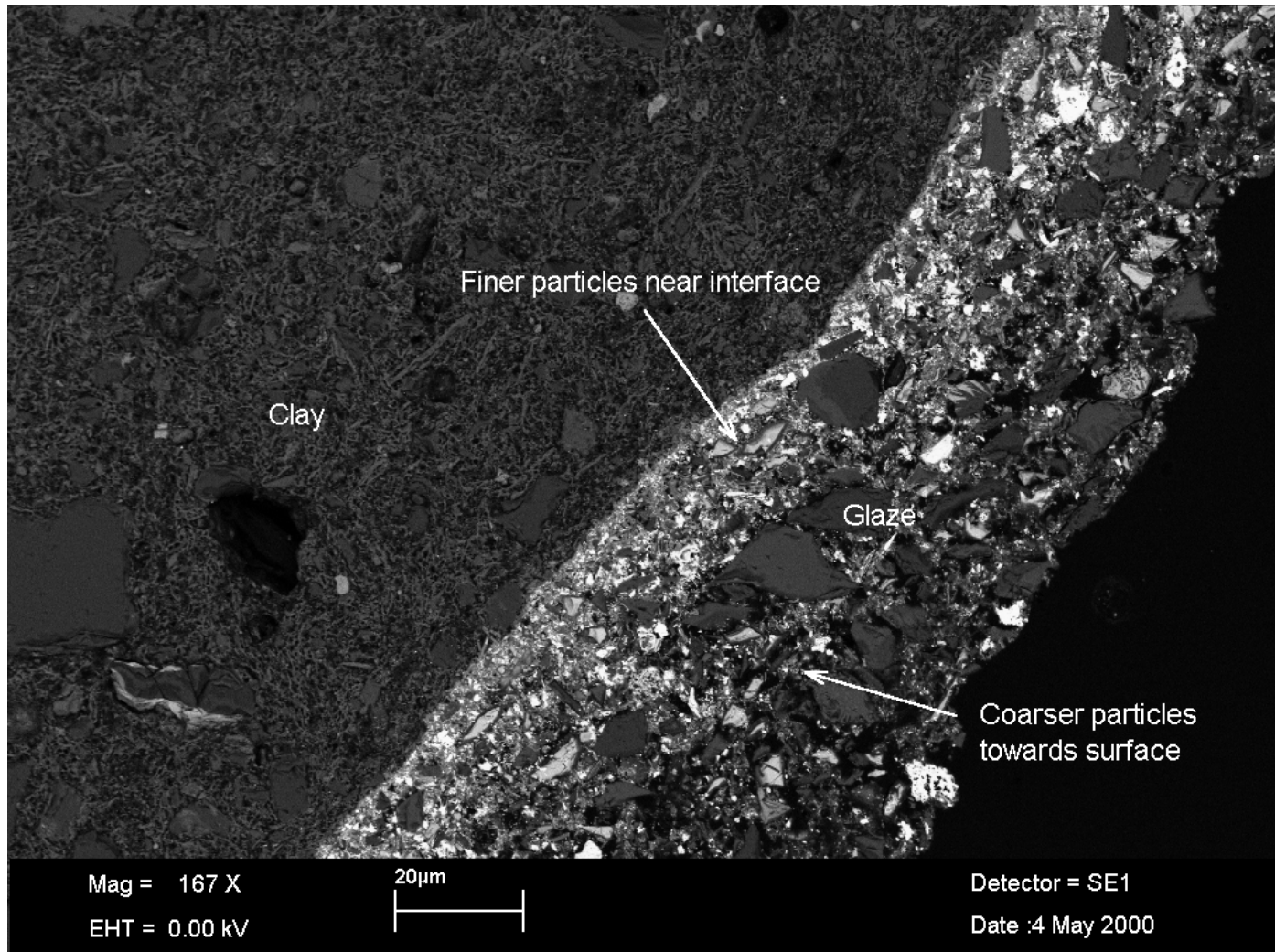


Figure 2

SEM back scattered electron image

