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Early porcelain in seventeenth-century England: non-destructive examination of two jars from Burghley House

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Summary This contribution focuses on the investigation of seventeenth-century porcelain from the collection at Burghley House, Stamford, Lincolnshire, using non-destructive scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDX) and Raman spectroscopy. The glaze and body of three seventeenth-century objects, a small jar, its lid and a larger jar, were analysed by SEM-EDX using the variable pressure (VP) mode to allow the surface of the jars to be examined directly and without damaging these objects by the need to take samples. Both this new application of direct VP observation and analysis of ceramic vessels and the limits of the method are discussed, as well as the possibilities for obtaining results that are directly comparable to those acquired by standard methods that require intrusive sampling.

The EDX analyses of the bodies of the two jars suggest that they were produced using a similar paste, high in clay content, while analysis of the lid suggests that it was made using a different paste, perhaps at a different time or by a different artisan; this mismatch is supported by differences in decoration and the poor fit between lid and jar. The glaze analyses indicate variable concentrations of lead, which may partly derive from the pigments and variations in the thickness of the glaze. The pigments used to decorate the small and large jars were also studied by Raman spectroscopy, indicating the use of haematite.

The results from the two jars show that the porcelain is different to that produced at Fulham by John Dwight and in Dehua as 'blanc de Chine'.

INTRODUCTION

Porcelain was first made in China in the sixth century AD [1]. Since its arrival in Europe in the fourteenth century, this beautiful, translucent, glassy and expensive product became a prestigious and luxurious item for European collectors [2]. From the sixteenth century onward in many European countries, such as Italy, France, Germany and England, much energy and capital were invested in trying to pursue the secret of the 'Arcanum' [3].

As Freestone has noted [3; p. 19], imperial Chinese porcelain was made from a mixture of kaolin and the porcelain stone *petuntse*, containing mica, feldspar and quartz, which was then fired at high temperature. Dehua porcelain was made of porcelain stone "without kaolin addition" and in which "the iron oxides levels ... could be as low as 0.2%" [4; p. 69].

The composition of early English porcelains has been studied in recent decades [3, 5–7], and one of the main

questions concerning the jars from Burghley House that are the subject of this study was of what type of porcelain they are made; that is, whether they are 'soft paste' or 'hard paste' (although the use of these terms can be problematic). True hard-paste porcelain was made from a mixture of feldspar (china stone) and a clay derived from the decomposition of feldspar (china clay). This porcelain was imported into Europe from the Jingdezhen region in Jiangxi Province, China and from the Dehua region in southern China. Hard paste was eventually manufactured in Europe, initially at Meissen in c.1720 [8].

This contribution compares the composition and manufacture of some porcelain vessels from the Burghley House collection with known (published) porcelains from China and Britain to determine their most probable place and date of manufacture. The paper also examines the application of variable pressure (VP) scanning electron microscopy (SEM) for the direct microscopic examination of large non-conducting vessels. The associated *in situ* energy



FIGURE 1. The two Burghley House porcelain jars and lid, the larger being the 'Virtues jar'. The elegant decoration is from a palette of red, green, black and gold

dispersive X-ray spectrometric (EDX) analysis of existing fractured surfaces on the porcelain and glazed surfaces is fundamental to their characterization, but in VP mode (compared to conventional high vacuum SEM analysis of carbon-coated materials) there are certain analytical characteristics that require critical evaluation to ensure that the analyses are accurate, consistent and comparable to conventional EDX analysis. In particular, the effects of electron beam 'skirting' (scatter), due to the presence of the controlled trace of air in the SEM needed to be studied to ensure the correct working parameters for this analytical approach are fully understood for future routine application of direct analysis in the VP-SEM-EDX.

THE BURGHLEY HOUSE JARS

The Burghley House porcelain vessels chosen for this study are the so-called 'Virtues jar' (height *c.*75 mm), named for the allegorical scenes painted in three medallions, and a small jar and cover decorated with putti and scrolls (height *c.*44 mm), which is one of a pair, Figure 1.

Both pieces are important because of their early date. They can be traced in the Devonshire Schedule of Deed, drafted in 1683 and proved in 1690 after the death of Lady Elizabeth Cavendish, the mother-in-law of the fifth Earl of Exeter [9; p. 20, 10]. This document is at Burghley House,

Lincolnshire, where the vases have been kept since at least around 1690, prior to which they were at Chatsworth House, Derbyshire. In later documents the vases have been described as 'the Duke of Buckingham's china'. Although it is not currently possible to attribute them firmly to any English factory, their English origin is thought likely. The decoration is dissimilar to that found on any other known porcelains apart from a related vase in a private collection. Both the three allegorical scenes on the 'Virtues jar' and the heads on the smaller jar are consistent with a date in the second half of the seventeenth century.

The main research objectives were to identify the chemical composition of the three objects, to see whether there are similarities or differences between them, as well as clarifying whether the lid originally belonged to the small jar.¹ In particular, the analyses aimed to determine the type of porcelain body and the nature of the glaze and colorants.

For curatorial reasons at Burghley House, the time available to study the jars was restricted, and it was therefore necessary to employ techniques that could be implemented rapidly. The objects were first studied by reflected light microscopy, to locate suitable areas of white paste, coloured decorated areas and existing fractured surfaces, before studying their chemical composition by SEM-EDX. The Virtues jar paste could be analysed at an existing crack on the side of the vessel, and at a chip on the rim (Figures 2 and 3), while chips on the small jar and lid offered sites for analysis.

METHODS

Only non-destructive analytical techniques could be considered. The natural choice to conduct qualitative and quantitative analyses and microstructural observation and photomicrography was the Museum's new VP-SEM, a Hitachi S-3700N. This instrument allows high-magnification images to be produced (from 7× to several thousand times), using a focused scanned electron beam. It is used in combination with the Oxford Instruments INCA energy dispersive X-ray spectrometer for quantitative elemental compositional analysis. The Hitachi S-3700N has two main advantages over previous SEMs for the study of porcelain. First, it has a large specimen chamber, allowing objects up to 200 mm in diameter and 65 mm high to be examined; these can be stood on the specimen stage, or laid on their sides if they are too high. Secondly, the VP mode enables a wide range of non-conducting samples (for example, pottery, ceramics, wood, glass, bone and other organic materials) that cannot be examined in a conventional high vacuum SEM to be studied at a range of voltages without being coated with a thin layer of carbon or gold [12]. A controlled amount of air is introduced into the vacuum chamber at low pressure (in the range 6–40 Pa) to counteract charge build-up on the sample surface, which would otherwise prevent observation and analysis.

The paste and glaze of the two jars and the lid were analysed to identify compositional similarities and differences. The 17 or 18 elements representing the range of characteristic ceramic constituents, opacifiers and colorants (Na, Mg, Al, Si, P, K, Ca, Ti, Mn, Fe, Pb, Ba, Sb, Sn, Cu, and S, with Au and Hg in cases where gilding is present) were quantified. The results were converted into oxide percentages (oxygen by stoichiometry) and normalized to account for not measuring oxygen and carbon. Glass standards were used for the analytical calibration and standardization of the system. To ensure that the bulk analyses were representative of the material, replicate analyses were generally made on three to eight areas (depending on the size of the object or fractured surface) and the mean values determined. The analyses were typically made at an SEM image magnification of 50–90×, selecting areas of $c.1 \times 1.5$ mm ($c.0.2 \times 0.4$ mm for associated homogeneous glazed layers) for bulk analysis within these images. Spot analyses (with a diameter of $c.5 \mu\text{m}$) were only made to identify particular small constituents or thin layers.

To minimize any scattered signals, the objects were mounted on a graphite plate that was attached to the large SEM stage and placed in the specimen chamber, Figures 2 and 4. Particular attention was paid to the orientation of the object or fracture section in order to position the areas to be analysed as close as possible to the ideal geometry for analysis, i.e. normal to the electron beam to give the appropriate take-off angle for the X-ray detector (30°), and with any potential regions of scatter on the object, such as the curved sides of the jar, pointing away from the X-ray detector.

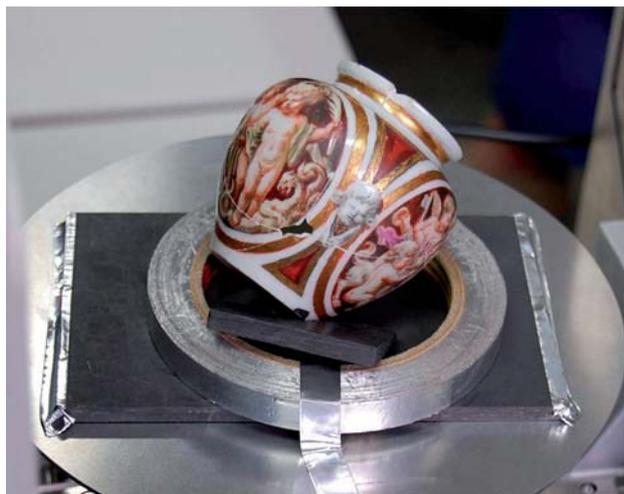


FIGURE 2. The large Burghley Virtues jar resting safely on a graphite plate on the large x-y stage of the VP-SEM. The existing crack on the side of the vessel where a fragment is missing (detail in Figure 3) and a chip on the rim are where the analyses were made

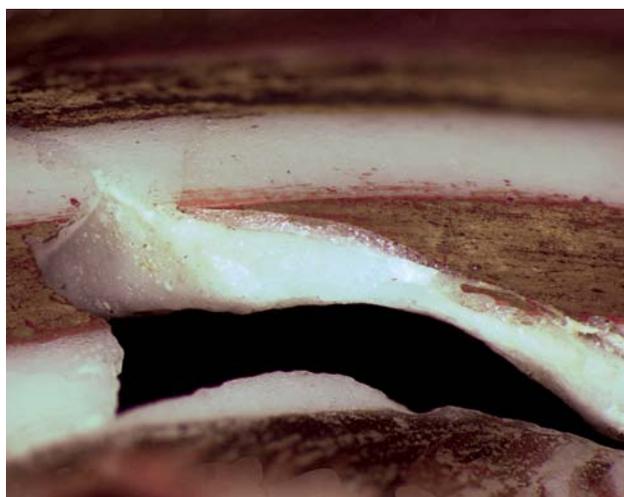


FIGURE 3. Reflected light microscope montage-image (40×) featuring the fractured hole in the side of the large Virtues jar. This has clearly exposed a cross-section of the white porcelain and the transparent surface glaze, which allows direct VP-SEM study and analysis



FIGURE 4. The Hitachi S-3700N Variable Pressure SEM used for the porcelain examination. The large jar is on the sample stage ready to be inserted into the very large sample chamber. The analytical X-ray detector is the blue device on the left side of the chamber. There are two large high-resolution imaging screens, one displaying the visible image of the pot

Instrumentation parameters

Prior to analysis of the Burghley jars, various experiments were undertaken to assess the accuracy of quantitative analysis by VP-SEM-EDX on fractured, unpolished or uncoated samples and objects that could potentially give unexpected or inaccurate results when compared to polished and coated thin sections – the ‘ideal samples’ for a conventional SEM. An example of such a difference is the so-called ‘skirting effect’, created by the interaction of the electron beam with the low air pressure in the chamber, which can cause a small proportion of the electrons to scatter outside the area of analysis.

These empirical measurements were intended to establish the practical working conditions and potential for direct, non-invasive VP-SEM examination and analysis, methods that have previously been impossible on large ceramic objects.

Raman spectrometry

Attempts were made to analyse the pigments in a number of the coloured areas under the glaze of the large and small jars using Raman spectrometry. The size and shape of the pieces meant that it was only possible to carry out this investigation non-invasively by using the horizontal side arm of the spectrometer, which can be difficult to focus.

ASSESSMENT OF ACCURACY OF VP-SEM-EDX

The analyses were made with the SEM at 20 kV, which is the usual voltage for ceramic analysis. Measurements were made at various working distances to cover the range of possibilities that might be used in future examinations of fractured objects.

The skirting effect

Examination of non-conducting materials and samples such as porcelain by VP-SEM simply requires a very low pressure of air to be admitted and maintained in the vacuum chamber to neutralize the electron charge at the surface of the material, and consequently allow microscopic observation, microphotography and analysis to be carried out.

In VP-SEM, most of the electron beam remains coherent and fully focused, allowing high-resolution imaging and analysis. A small proportion of the primary electron beam is, however, scattered in a conical fashion as the beam passes through the air before reaching the object surface – this is the skirting effect [12].

Ideally, the minimum pressure that neutralizes the electron charge should be used, so a range of pressures

from 6 to 100 Pa was tested. At lower pressures skirting is reduced but charging may occur, while at higher pressures skirting will increase, reducing the image resolution. Extensive use of the system at 20–30 Pa proved most satisfactory and this is now established as the normal working range for most ceramic examinations.

Tests on polished ceramic thin sections framed with copper strips

At the normal analytical working distance of 10 mm, it was possible to analyse the ceramic thin section as close as 1 mm from the copper test strip with no observable copper peaks in the spectrum. While analysing the same area with a 20 mm working distance, only a small peak for copper due to skirting was observed. When fractured sherds of porcelain or pottery are analysed, the sherd wall stands vertically with the fractured edges, which are typically up to several millimetres thick, horizontal. In this orientation the effects of skirting, and consequently the contribution of extraneous analytical information, are at best not seen and at worst are minimal and can be further reduced by adjusting the orientation of the object or even by masking an area with removable thin carbon tape. For the surface examination of decorated porcelain pots, consideration is given to potential skirting effects when analysing different coloured glazes or pigmented areas to ensure that extraneous signals from adjacent colours do not affect the results.

Comparison of analyses on uncoated fractured and uncoated polished samples: Dehua (blanc de Chine) porcelain samples

To identify any differences that might occur between the results obtained from analysis of an uncoated fractured sample in the VP-SEM and analysis of an uncoated polished section of the same material, the fractured edge of a fragment of a small bowl from the Jaibei old kiln site in Dehua and a polished thick section from the same bowl were analysed in the Hitachi S-3700N in VP mode at a pressure of 30 Pa, Figure 5. Three bulk analyses of the paste and the glaze were carried out on the unpolished fracture sample and the results averaged. Given the homogeneity of the polished sample, and proven reproducibility of the analyser, only one bulk analysis was carried out on both paste and glaze. Encouragingly, the results from the paste of the fractured, unpolished sample are virtually the same as those from the polished section, Table 1. The glaze in the unpolished sample shows higher silicon content (SiO_2 : 68.6 versus 66.0%) and lower calcium content (CaO : 7.2 versus 9.4%) than the glaze in the polished section; as the glaze is a very thin layer, this is perhaps due to the orientation of the sample.

Comparison of analyses on polished coated and uncoated samples

Comparing the composition of the polished Dehua porcelain sample analysed uncoated in the VP-SEM with the same sample carbon-coated and analysed in the high vacuum Hitachi S-4800 field emission scanning electron microscope (FE-SEM) gave the same results within statistical analytical errors. This is to be expected, as the absorption of the emitted X-rays by the residual air in the VP chamber is negligible at this very low pressure (30 Pa), Table 1.

Reproducibility

Reproducibility between repeated analyses both on fractured sections and polished samples was below 0.2%. For example, three consecutive analyses on different fracture areas on a sample of Dehua porcelain, gave the following data for the three most abundant oxides: SiO₂ 73.3, 73.7, 73.5%; Al₂O₃ 19.6, 19.7, 19.8%; K₂O 5.9, 5.7, 5.8%.

Analytical accuracy of fractured ceramics versus polished samples: the Eccles porcelain samples

Some English porcelain objects from the Eccles collection, which had already been extensively studied [13], were lent to the authors by the Victoria and Albert Museum. The analysis of five of these objects is considered in [7; appendix]:

- A saucer, decorated in polychrome enamels, made in Bristol; c.1775; catalogue number C352-1903; here referred to as Eccles 2; English hard paste.
- A fragment of a white coffee cup with applied sprays of *Prunus*, made in Bow; c.1765–1770; C590-1919; Eccles 12; bone-ash paste.
- A fruit dish in the form of a cabbage leaf decorated in underglaze blue made in Bow; c.1765–1770; C16-1920; Eccles 14; bone-ash paste.
- A saucer decorated in underglaze blue and enamels, made in Lowestoft; c.1770–1775; C638-1920; Eccles 16; bone-ash paste.
- A fragment of a tea cup decorated in underglaze blue, made in Worcester; 1760; C591-1919; Eccles 26; soap-stone paste.

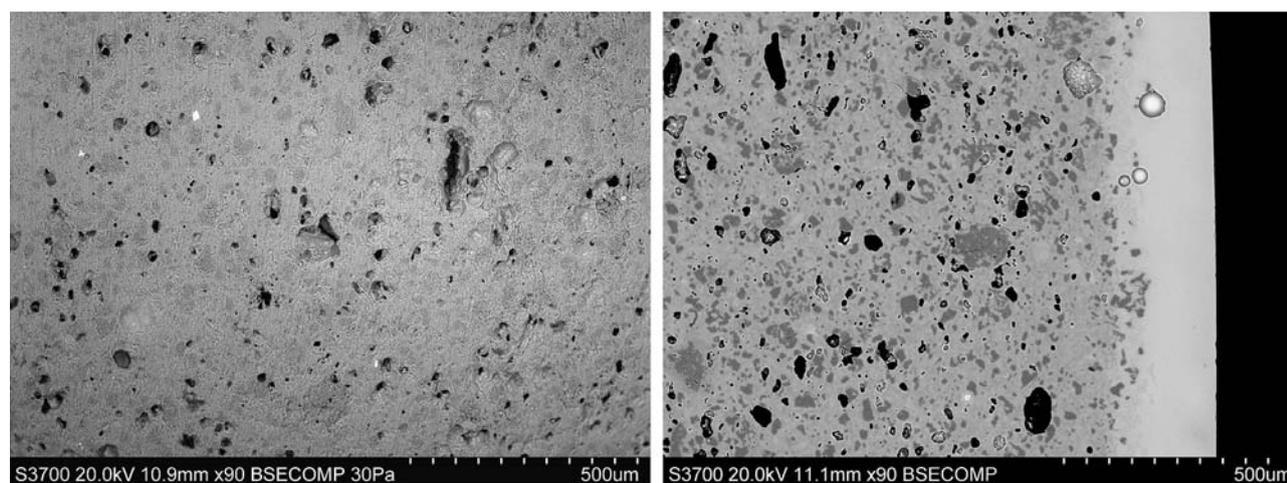


FIGURE 5. SEM image of the Dehua porcelain samples: comparison between the fracture surface of the paste, left (lightly abraded), and polished section, right, including the surface glaze. The polished section clearly shows (by atomic number contrast) the mineral phases that form during firing of the porcelain, which do not show in the fracture section. However, the composition comparison between the two sections is similar

TABLE 1. EDX analytical results for Dehua porcelain, reported as normalized oxide percentages as described in the text. Area analyses are typically made at a SEM image magnification of 90–350× by selecting bulk areas for analysis within these images of around 1 × 1.5 mm, down to 0.2 × 0.4 mm on associated homogeneous glazed layers

Sample	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	TiO ₂	MnO	FeO	SnO ₂	BaO	PbO
Paste; fractured and uncoated; average of 3 bulk analyses; 90×	0.1	0.2	19.7	73.4	0.0	0.0	5.8	0.3	0.1	0.1	0.2	0.2	0.0	0.0
Paste; uncoated polished section; 30 Pa	0.1	0.2	19.0	74.2	0.1	0.1	5.7	0.2	0.0	0.0	0.2	0.1	0.1	0.0
Paste; coated polished section (same area as above); bulk; 90×	0.1	0.2	19.0	74.2	0.1	0.1	5.8	0.2	0.1	0.0	0.2	0.1	0.1	0.0
Glaze; fractured and uncoated; average of 3 bulk analyses; 100–350×	0.2	0.8	16.0	68.6	0.4	0.1	5.6	7.2	0.0	0.3	0.2	0.5	0.2	0.0
Glaze; coated polished section; bulk; 90×	0.2	0.7	16.0	66.0	0.4	0.0	6.3	9.4	0.0	0.4	0.2	0.4	0.3	0.0

In all 26 bulk and spot analyses were conducted on both the paste and the glaze at fractures in these objects. The results obtained on the paste using the VP-SEM (Table 2) are similar to the results published by Tite and Bimson on carbon-coated polished samples analysed under high vacuum [7; Table 1]. Most of the data are very similar, except for the sample from Eccles 2, where some lead was detected in the glaze (3.9%) that was not detected by Tite and Bimson, but was reported by Eccles [13; p. 23]. The other major oxides, however, such as those of aluminium, silicon, potassium, phosphorus and calcium, show very similar results. In the present analysis, the sample from Eccles 12 shows a higher percentage of Al₂O₃ and less SiO₂ than in the previous analyses by Tite and Bimson [7]. There appeared to be a small difference in the SiO₂ concentration, which was around 2% less in some of the fractured samples compared to the polished samples. The reproducibility of the measurements on the fractured samples was good, so it might be that this variation is associated with the greater porosity or roughness of these samples compared to the more solid Dehua porcelain.

ANALYTICAL RESULTS FOR THE BURGHLEY HOUSE JARS

The Virtues jar

The SEM produces backscattered electron images (Figures 5–8) that show a high degree of atomic number contrast,

rendering the variation in elemental composition visible at high magnification. The reflected light microscopic image (Figure 3) is complemented by the SEM images of the crack on the side of the Virtues jar (Figures 7 and 8) that clearly show the complex layered structure above the hole. This comprises the fractured paste, a crack just below the interface with the glaze (which contains gas bubbles), various areas of colourless or pigmented glaze and surface gilding.

The glaze was analysed by making 17 bulk analyses on four different areas, typically at an SEM image magnification of 50–90× and by selecting bulk areas for analysis within these images of between 1 × 1.5 mm and 0.2 × 0.4 mm on the exposed interior crack surfaces. The samples were: the exterior of the glaze on the curved surface near the rim (five bulk analyses); two larger colourless transparent areas (two bulk analyses); the interior of the glaze exposed in the crack/fracture (five bulk analyses); the top of a fresh fracture on the side of the vessel (one bulk analysis); and the sub-surface of the glaze, where it appeared to have been abraded (four bulk analyses). The gilding was also studied through one bulk analysis made on an area of 0.02 × 0.02 mm at high magnification.

The glaze on the curved rim is rich in silicon, aluminium and calcium, has relatively high potassium and lead, and is low in sodium, magnesium and iron. The results from the fracture and colourless areas seem to be less homogeneous, probably due to the geometry of the areas studied; the data are similar to those obtained from the rim, but with some gold content. The colourless areas show an increase in lead and very low quantities of calcium. Lead and iron are very unevenly distributed, showing variation throughout the

TABLE 2. EDX analytical results for Eccles porcelain, reported as normalized oxide percentages as described in the text. Area analyses are typically made at a SEM image magnification of 90–150× by selecting bulk areas for analysis within these images of around 1 × 1.5 mm, down to 0.2 × 0.4 mm on associated homogeneous glazed layers

Sample	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	SnO ₂	Sb ₂ O ₃	BaO	PbO
Paste; Eccles 2; 3 bulk analyses; 90×	0.8	0.2	25.4	69.8	0.2	0.0	2.7	0.3	0.0	0.0	0.5	0.0	0.0	0.0	0.0	0.0
Paste; Eccles 12; 3 bulk analyses; 90×	0.5	0.5	6.7	42.7	17.8	3.2	0.8	26.0	0.3	0.0	0.4	0.1	0.6	0.0	0.2	0.3
Paste; Eccles 14; 2 bulk analyses; 90×	0.7	0.5	6.7	43.0	19.8	3.4	0.6	23.6	0.3	0.0	0.3	0.0	0.5	0.0	0.0	0.3
Paste; Eccles 16; 3 bulk analyses; 90×	0.8	0.7	7.6	38.9	20.0	0.5	1.0	28.3	0.3	0.0	0.6	0.0	0.7	0.0	0.2	0.3
Paste; Eccles 26; 6 bulk analyses; 90×	1.3	10.9	5.5	69.9	0.4	0.7	2.7	2.1	0.2	0.1	0.9	0.0	0.2	0.0	0.0	5.2
Glaze; Eccles 2; 3 bulk analyses; 90×	1.8	2.8	17.0	63.1	0.8	0.0	3.4	3.7	0.2	0.1	1.6	0.4	0.6	0.0	0.0	5.0
Glaze; Eccles 12; 4 spot analyses	0.5	0.2	1.1	43.4	0.7	0.5	3.9	2.2	0.0	0.0	0.1	0.1	1.5	0.0	0.0	45.6
Glaze; Eccles 12; 2 bulk analyses; 90×	0.6	0.2	0.9	45.3	0.0	0.3	3.8	0.5	0.0	0.1	0.0	0.0	1.0	0.0	0.1	46.4
Glaze; Eccles 14; 3 bulk analyses; 150×	0.5	0.2	0.8	43.1	0.3	0.0	4.0	1.2	0.0	0.1	0.3	0.2	1.7	0.0	0.0	47.6
Glaze; Eccles 14; 3 bulk analyses; 150×; replicate	0.5	0.1	1.1	44.9	0.3	0.4	4.2	1.0	0.0	0.0	0.1	0.0	2.2	0.0	0.2	44.8
Glaze; Eccles 16; 3 bulk analyses; 90×	0.7	0.1	1.4	44.3	0.5	0.0	3.5	2.7	0.0	0.3	0.2	0.1	0.1	0.0	0.0	46.0
Glaze; Eccles 26; exterior surface; 2 bulk analyses; 90×	1.9	3.1	4.5	55.1	0.0	0.1	2.8	1.0	0.0	0.0	0.4	0.1	0.2	0.0	0.1	30.7

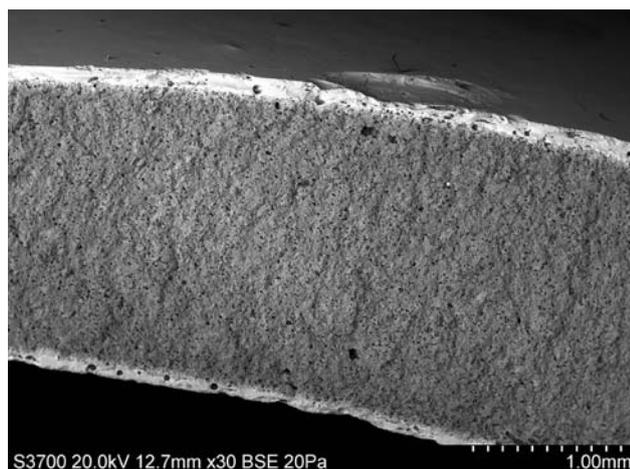


FIGURE 6. SEM image of the fracture section of one of the Eccles large porcelain fragments. Note the homogeneous, fine texture of the fractured paste and the lead glaze layer on the surface clearly distinguished as a lighter band due to the atomic number contrast of the lead in the glaze

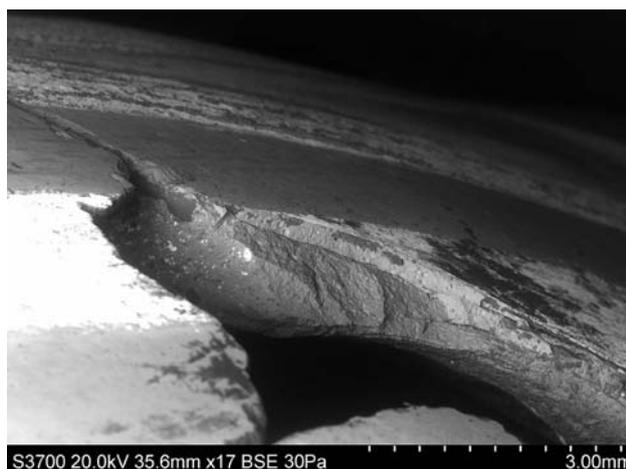


FIGURE 7. SEM image of the fractured hole seen in Figure 3, showing the various structures with good depth of focus. The fracture area shows the textured porcelain paste, lower centre, with the thick glaze layer above. The smooth curved surface is the colourless glaze on the porcelain. The light surface band to the left is an area of gilding

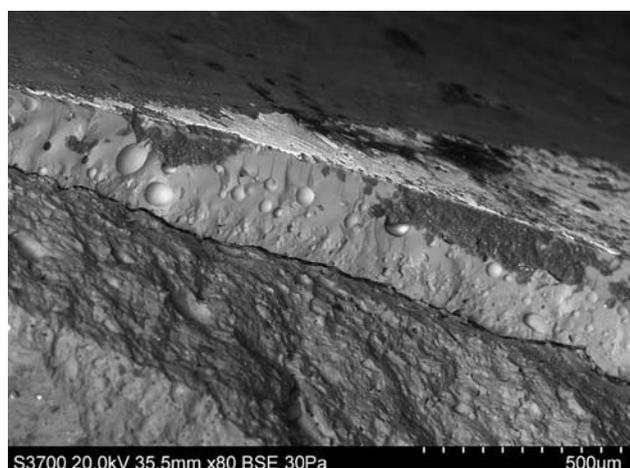


FIGURE 8. SEM detail of the fracture on the large Burghley jar showing the textured fractured paste in the foreground, the thick glaze above with spherical gas bubbles exposed at the fracture. An interdiffusion zone that is visible in the lower quarter of the glaze shows the fine texture of the crystalline minerals formed during firing and a fracture line is seen between this interdiffusion zone and the paste. Surface gilding is seen as the thin light surface layer. Note that there is no sign of charging in this image, which was made with a SEM chamber pressure of 30 Pa

vessel surface, Table 3. The thin glaze has rather high and variable gold content, most probably due to the dissolution of gold from the gilding into the glaze during the firing process. The gilding composition is 98% gold and 2% silver, indicating that high purity gold was applied to the surface and fused to the glaze.

The paste of the jar was analysed in the chip on the rim (six bulk analyses) and in the crack (one representative bulk area analysis on an area of 0.5×0.5 mm, Figure 8). The results indicate a largely homogeneous composition, rich in silicon and aluminium, low in calcium, with the potassium predominant over sodium and with some magnesium, titanium and iron; lead is also present at low concentrations.

Raman analysis identified the red pigment used in the figures on this larger vase as haematite. This was detected in the black/red interface above the wing, the dark red area of the lozenge, and the flesh colour of the putto, Figure 1. Attempts to analyse green areas on the large jar and black areas on the small jar produced only spectra for quartz (SiO_2).

The small jar

The glaze of the small jar was analysed on the rim (two bulk analyses at $150\times$) and on the interface between the paste and the glaze (one bulk analysis at $800\times$). The paste of the jar was studied where the glaze was missing with three bulk analyses at $150\times$. The gilding was studied with three spot analyses at $800\times$.

The glaze on the rim shows high silicon, lead and aluminium contents, and rather low calcium, potassium, iron and sodium. The interface between the paste and the glaze shows different percentages of oxides, with higher silicon, aluminium and potassium, and a lower lead content. The results for the major oxides in the paste are similar to those for the Virtues jar, with high silicon and aluminium contents, but lower iron, titanium and magnesium. As with the Virtues jar, lead was detected in the paste and the gilding had been produced using almost pure gold ($>94\%$).

Element distribution mapping was tested on the coloured decoration on the small Burghley vase as a potential method for analysing the coloured glazes or pigmented decoration directly on porcelain. Figure 9 shows a false-coloured X-ray map for iron on the decorated shoulder of the small Burghley vase alongside an image of the vase itself. The iron concentration clearly follows the red-lined decoration, correlating well with the identification of haematite

TABLE 3. EDX analytical results for Burghley House porcelain jars, reported as normalized oxide percentages as described in the text. Area analyses are typically made at a SEM image magnification of 20–80× by selecting bulk areas for analysis within these images of around 1 × 1.5 mm, down to 0.2 × 0.4 mm on the exposed interior crack surfaces

Sample	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	SnO ₂	Sb ₂ O ₃	BaO	PbO	Au ₂ O ₃
Virtues jar; paste; 8 bulk analyses, chipped rim 50× and fracture on side 80×	1.6	1.5	18.2	66.8	0.0	1.6	4.5	0.6	1.2	0.1	1.1	0.1	0.3	0.1	0.1	2.2	
Small jar; paste; 3 bulk analyses; 150× and 350×	1.4	0.5	18.9	69.0	0.1	0.0	5.8	1.4	0.1	0.0	0.6	0.0	0.4	0.0	0.0	1.7	
Lid; paste; 8 bulk analyses; 60×	2.7	0.8	18.1	62.6	0.6	0.2	6.0	6.1	0.2	0.0	0.6	0.0	0.4	0.0	0.1	1.7	
Virtues jar; glaze on rim; 5 bulk analyses; 50×	1.4	1.3	13.2	59.6	0.2	0.0	4.1	10.1	0.0	0.3	2.6	0.0	0.6	0.4	0.1	6.2	
Virtues jar; colourless glaze; 2 bulk analyses; 20×	1.6	1.4	1.0	29.9	0.1	1.4	1.3	1.4	0.3	4.9	5.1	3.7	1.1	0.7	0.9	44.3	
Virtues jar; glaze near fracture; 3 bulk analyses; 80×	1.5	1.2	13.3	65.8	0.2	0.1	3.4	7.6	0.1	0.2	1.2	0.1	0.4	0.1	0.1	4.9	
Virtues jar; thin glaze; 2 bulk analyses; 200×	1.1	0.8	11.7	57.3	0.3	0.0	3.3	7.6	0.0	0.0	1.9	0.0	0.2	0.2	0.0	6.7	9.0
Small jar; glaze; 3 bulk analyses; 150× and 350×	1.0	0.8	11.8	53.6	0.1	0.0	3.6	4.9	0.1	0.1	1.3	0.0	0.2	0.2	0.1	22.4	
Lid; pigmented glaze on edge of the lid; 1 bulk analysis; 35×	1.5	0.8	1.4	40.0	0.0	1.1	1.8	3.7	0.1	0.2	3.5	0.3	0.4	0.0	0.0	45.5	
Lid; colourless glaze on edge of the lid; 1 bulk analysis; 35×	3.1	1.4	10.6	53.4	0.3	0.8	4.5	11.5	0.0	0.2	2.1	0.0	2.6	0.6	0.3	8.5	
Lid; thin glaze under area interface; 1 bulk analysis; 1000×	1.9	1.6	11.9	53.2	0.4	0.8	3.7	15.1	0.1	0.2	1.1	0.1	1.8	0.7	0.3	7.0	

as the red mineral pigment used in the coloured glaze by Raman analysis. Presumably the red-coloured glaze mixture was painted onto the white porcelain and then fired to fuse the glaze. Mapping can easily be used to see the differences between coloured minerals in glazes as well showing the contrast between gilding and leaded glazes compared to unleaded pastes.

The lid

The glaze of the lid was analysed at the interface between the glaze and the paste (one bulk analysis at 1000×), on the transparent glaze on the edge (one bulk analysis at 35×) and the coloured glaze on the edge (one bulk analysis at 35×). The paste was analysed in two areas of the chip (three bulk analyses at 60× and three spot analyses).

The results from the glazed areas gave a wide range of values, particularly for the oxides of lead (7–45.5%),

calcium (3.7–15%), iron (1.1–3.5%), magnesium (0.8–1.6%) and sodium (1.5–3.1%). The paste has high aluminium and silicon contents, is rather high in potassium, calcium and sodium, and has low manganese, titanium, and iron contents. Finally, in common with the pastes of the two jars, some lead was detected.

DISCUSSION

Some valuable results were obtained despite the use of less than ideal samples and the limited time available for analysis. A wide range of oxides was considered for these analyses, but it is clear that the two seventeenth-century jars were produced using similar raw materials, with high silicon and aluminium contents, low calcium content and with potassium predominant over sodium. It should be noted that the lid has a different composition, with higher

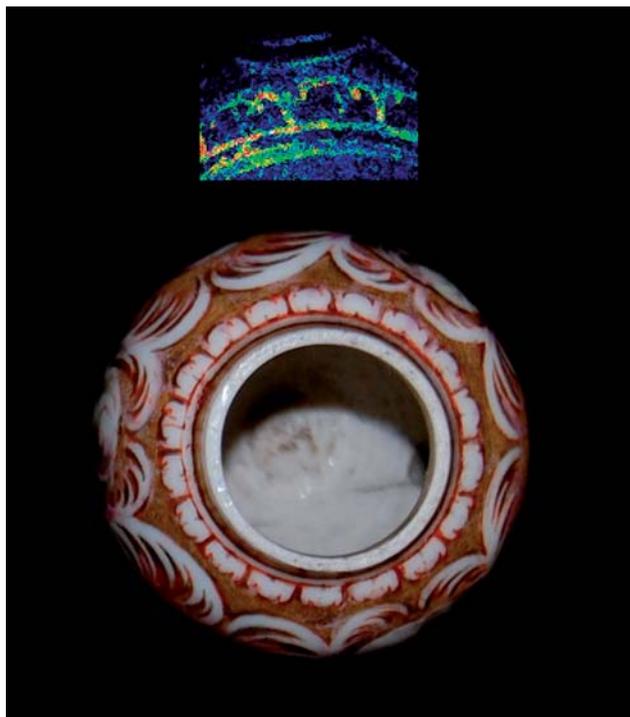


FIGURE 9. The small Burghley jar seen from above showing the red and gold decoration in the glaze. Superimposed above the image is an analytical X-ray distribution map of iron on an area of the decoration on the shoulder, showing that the pigmented glaze corresponds to the finely painted red lines on the porcelain

contents of sodium (2.7% versus 1.6 and 1.4% for the large and small jars respectively) and calcium oxides (6.1% versus 0.6 and 1.4%), see Table 3.

The glazes on the three objects show variable concentrations of lead, which may partly derive from the pigments, or from diffusion during firing, as lead is mobile at high temperatures. This may also account for the presence of lead in the pastes, as all three objects were coated with a lead-rich glaze. The composition of the glaze on the lid, in particular, varies a great deal between sampling locations.

In both jars, the gilding has a very high gold content. The thin glaze also shows significant percentages of gold, probably due to the dissolution of the gilding into the glaze during the manufacturing process.

In this study, the microstructures of the fractures on both the jars and the lid showed that the porcelain bodies are clearly highly vitrified from high temperature firing and resemble a hard-paste body, with high clay content, negligible calcium with potassium predominant over sodium and low, but variable, levels of titanium and iron oxides (the low level of the last of these being responsible for the whiteness of the porcelain body). The highly vitreous paste seen in the fracture section of the Virtues jar (Figures 7 and 8) shows a physical texture that would indicate the presence of crystalline phases within the glassy matrix of the paste, compared to the smooth conchoidal fracture of the surface glaze alone. Hard-paste porcelain contains mullite crystals (a high temperature aluminium silicate) and sometimes crystals of unreacted quartz, suspended in an alkaline, lead-

free glass [7; p. 22]. In hard-paste porcelain there is no clear interface between the paste and the glaze, but in the Virtues jar a narrow inter-diffusion zone with mixed phases can be seen, Figure 8.

Although the Burghley House jars have a lead glaze more characteristic of soft-paste porcelain, they are not made of soft and glassy pastes, such as those developed in France and England in the mid-eighteenth century [7; Table 2 and pp. 10–13, 14; p. 79].

In seventeenth-century London, two types of porcelain would have been available to the decorator of these jars: that imported from Dehua in China and that made by Dwight at Fulham. EDX analysis of one fragment from the production site at Dehua indicated similar concentrations of aluminium and potassium as in the Burghley House jars, but higher silicon and lower levels of iron, calcium, magnesium and sodium.

Unlike oriental porcelain, which was made of so-called primary clay (china clay), Dwight's porcelain was made using a so-called secondary clay (ball clay), with a potash frit instead of the feldspar (china stone) found in oriental porcelain. Waste fragments (wasters) excavated at Fulham have been analysed [15], but none of these were fragments from smaller vessels that might resemble the Virtues jar. If such fragments could be studied, it would be possible to compare the results with those from the Burghley House material.

Although the Fulham fine white ware analysed by Tite *et al.* [15; pp. 98–99 and Table 9.1], was quite variable in composition, it was different to the Burghley House jars, with a lower aluminium content and higher levels of silicon and potassium, Table 3. Furthermore, the Burghley House jars show higher magnesium, potassium, iron and titanium contents.

The presence of lead in the paste of both the Burghley House jars is difficult to explain, but it might be due to contamination from the glaze since, as mentioned above, both jars have lead glazes and lead can be mobilized at high temperatures. However, neither the Dehua porcelain (which has a standard Chinese glaze of SiO_2 , Al_2O_3 and CaO) nor the Fulham porcelain has lead glazes [4, 15].

CONCLUSIONS

Variable pressure SEM has made it possible to carry out reliable, reproducible EDX analyses of acceptable accuracy on less than ideal fractured samples, provided the usual precautions are taken with sample geometry, the pressure used to counteract charging is minimized to reduce skirting effects and the porosity of the fractured material is low. The VP-SEM opens up new possibilities for the direct examination of the broken, chipped, or cracked areas that are often present on old objects; even repaired cracked vessels were safe in the vacuum chamber, with no movement of glued fragments observed.

The analyses of the Dehua and Eccles porcelains indicate that reliable results can be obtained without invasive sampling, provided that particular attention is paid to parameters such as the object geometry and the distance between the area analysed and the edge of the samples.

The results from the two seventeenth-century Burghley House jars show that they were made of a very similar paste, suggesting that they could have been made by the same workshop. A paste high in aluminium and silicon and low in calcium was used to produce the jars, and a slightly different paste was used to manufacture the lid of the small jar, possibly some time later. Haematite was used to obtain the red colour of the putti and the decorations on the background of the large jar. In all three objects, the lead content of the glaze is highly variable, perhaps because of mixing between the glaze and the pigments during firing. In the large jar, it was possible to see a narrow interface between the paste and the glaze.

Although jars of similar size to those from Burghley House were found during the excavation of the Fulham site [16; Figure 49 and p. 71], a combination of the chemical compositions of both paste and glaze, and stylistic features, suggest that the Fulham and Dehua factories were probably not the origin of these jars. In addition, Dehua porcelain rarely lacks handles, knobs or other protrusions and the paste of the Dehua porcelain that was studied is more vitrified than the paste of the Virtues jar, Figures 5 and 8.

The existence of another production centre that has not yet been studied could be considered, as the significant lead levels in both Burghley House jars do not correspond to any of the comparable results from Dehua or Fulham porcelains. While the lead content of the paste in the Burghley House jars may be due to contamination from the glaze, the very presence of such a lead glaze might indicate a hitherto unknown source.

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NOTE

- In 1991, the lid was analysed by X-ray diffraction (XRD) and X-ray fluorescence (XRF) by Middleton [11]. In the paste, only quartz was identified by XRD, and potassium, iron and lead (and possibly calcium) were identified by XRF. In the glaze, potassium, calcium, manganese and lead were identified.