

## Article

# Investigating Late Bronze Age Glass Beads from Stotfold, Bedfordshire, UK

Sarah Paynter <sup>1,\*</sup>  and Caroline M. Jackson <sup>2</sup> <sup>1</sup> Historic England, Fort Cumberland, Fort Cumberland Road, Eastney, Portsmouth PO4 9LD, UK<sup>2</sup> Department of Archaeology, University of Sheffield, Minalloy House, 10-16 Regent Street, Sheffield S1 3NJ, UK; c.m.jackson@sheffield.ac.uk

\* Correspondence: sarah.paynter@historicengland.org.uk; Tel.: +44-2392-856782

**Abstract:** A total of seventeen annular transparent blue glass beads and one cylindrical glass bead with opaque grey-white decoration were found at a site near Stotfold, in Bedfordshire, England. The beads were part of a cremation burial (without an urn), associated with small fragments of gold sheet and bone, and the latter were carbon dated to 1303–1052 calBC with 95% probability. Analysis (quantitative using SEM-EDS and qualitative using XRF) found that the beads are made from low magnesium, high potassium (LMHK) glass, of the type prevalent in Europe between around 1200 and 900 BC. The grey-white trail on the cylindrical bead is opacified in a novel way, as neither tin nor antimony colourants were used. These are only the second confirmed example of LMHK glass beads from England, and the earliest in date. They provide evidence of networks extending between this community and continental Europe in the Later Bronze Age, and the burial of a high-status individual at Stotfold. Experimental recreation is used to investigate the possible methods of making the glass, using plant ashes, copper oxide, and quartz sand. A multi-stage process is proposed, using a low temperature firing before the final high temperature melting and homogenising.



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**Keywords:** Bronze Age; glass; UK; analysis; LMHK; mixed-alkali

## 1. Introduction

Between 2007 and 2010, Albion Archaeology undertook archaeological investigations on c. 17.5 ha of land south of Stotfold, Bedfordshire. Most activity at the site was associated with settlement in the middle Bronze Age to middle Iron Age (c. 1500–100 BC), and again in the late Saxon to Saxo-Norman periods (c. 900–1100 AD) [1]. The earlier features included inhumations and cremations dating to the Later Bronze Age. One of these cremation burials, G613 within area L43, comprised calcined bone associated with fragments of a copper alloy tubular ring, a small piece of gold sheet and a collection of blue glass beads. There were seventeen wound annular beads in translucent blue glass, some malformed by heat and five badly perished, plus one cylindrical glass bead in translucent blue with opaque greyish white glass decoration. The majority of the beads were between 4.6 mm and 6.8 mm long, 4.6 and 6.1 mm wide, and 1.4 to 3.2 mm tall, and the largest annular example was 8.9 mm long, 7.1 mm wide, and 4.9 mm tall. The decorated bead was 10.6 mm long and 5.5 mm at its widest point with a series of whitish trails applied in bands, dragged upwards on one side and downwards on the opposing side, to create a chevron pattern (Figure 1).

Dating of two samples of cremated bone provided a Bronze Age date, with a radio-carbon age of BP 2905 ± 30 or 1220–1000 calBC, and BP 2960 ± 35 or 1303–1052 calBC at 95% probability [1,2]. However, Bronze Age glass objects are very rare in Britain, so chemical analysis was used to establish beyond doubt the association of the beads with the cremation burial and confirm their early date. The chemical composition also provides information on the origins of the beads, as similar examples were made in many different parts of the world at this time and were widely transported [3]. A sample was taken from only one of the beads, and selected others were analysed using non-destructive means to

determine whether they were of the same glass type. The results are an important addition to an otherwise small dataset for Bronze Age glass artefacts in England.



**Figure 1.** The decorated bead <568> (rear left), and two of the annular beads <575> (right) and the weathered bead <584> (front left). Bead <584> was sampled for analysis.

### 1.1. Bronze Age Glass

Glass beads have been found previously from Bronze Age contexts in the UK and Ireland, but usually in small numbers and of uncertain date. They are more often found with funerary deposits and very occasionally on settlement sites [4–6]. The notable exceptions, where large numbers have been found, are the ringfort at Rathgall, Co. Wicklow, Ireland, where in excess of 70 mostly turquoise blue-green beads were assigned to 1150–1000 BC (this a recently revised date, earlier than that given when the beads were originally published); Lough Gur, Co. Limerick, Ireland, where around 30 beads were found of uncertain date; and the Late Bronze Age pile-dwelling site at Must Farm in Cambridgeshire, where at least 80 glass beads have been recovered [3,4].

However, there is a broad distribution of similar beads in continental Europe, and evidence for fairly large-scale production of glass beads towards the end of the Bronze Age (1200–900 BC) [7]. In Italy, indications of glassmaking from raw materials, and more commonly of glassworking, have been found at Frattesina and the surrounding area, in Northern Italy, together with remnants from many other crafts, including copper alloy casting [8]. This glassmaking and working are thought to date largely to the 11th and 10th centuries BC, and include opaque red, opaque dark blue, and transparent light blue glass [9]. Glassmaking follows on from long-established faience-making in the region, which can be traced back to the Early Bronze Age [8,10].

### 1.2. Glass Compositions

Distinctive compositions of glass dominate in different regions and chronological periods because of changes to the raw materials and methods used in their production [3,8–11]. For blue glass in the Late Bronze Age, such as the Stotfold beads, there are several possibilities, each made with different raw materials:

- Soda plant ash glass or high-magnesium glass: A soda-lime-silicate glass made from soda-rich plant ashes, which also contains several weight percent each of potassium and magnesium oxides [6,8,12,13];

- Low-magnesium, high-potassium glass (abbreviated to LMHK) or mixed-alkali glass: A potassium-rich glass that may contain equal amounts of sodium but only low levels of magnesium [6,12];
- Natron glass or low-magnesium glass: A soda-lime-silicate glass containing very little magnesium or potassium oxides, made using a type of mineral soda, particularly sourced from Egypt [9,14,15].

## 2. Materials and Methods

### 2.1. Analysis of Beads and Experimental Melts

A small fragment, approximately 2 mm wide, was removed from one of the plain annular beads, small find number 584, mounted in resin, polished and carbon coated, and examined using an FEI Inspect F scanning electron microscope (SEM) with attached X-act energy dispersive spectrometer (EDS) with INCA software, at 25 KeV. Permission was given to sample this single bead on the basis that it was already fragile. Sampling exposed fresh glass for analysis, as the surface will be chemically altered by heat during the cremation process and by weathering. Both of these processes affect the alkali content of the glass surface, in particular sodium is depleted, and potassium may be increased [16]. Using the SEM, unaltered areas of glass from the core of the bead were visually selected for analysis, so the values for sodium obtained by the EDS analysis method are more likely to be representative of the original glass. The results were quantified as stoichiometric oxides and normalised to 100 wt% (the totals were between 96 and 99 wt% before normalisation). A total of two Pilkington standards, which mimic a high soda and high potash glass, were also analysed to determine the accuracy and precision of the results (Table 1). Detection limits were 0.1 wt% for most oxides, but slightly greater at 0.3 wt% for chlorine and the oxides of sulphur, phosphorus, tin, antimony, and cobalt. Samples of the experimental melts were mounted and analysed with the same methods as for the archaeological material.

**Table 1.** Composition of bead <584> (4 analyses by SEM-EDS of one sample), sulphur, lead, antimony, chlorine, cobalt, and manganese were sought but not detected (bd = below detection limit), normalised (original totals shown in italics in final column), plus average of 2 analyses (anl) for Pilkington glass standards CL330 and CL324, against their reported (rpd) compositions (Pilkington European Technical Centre pers. comm.) (- = not present).

| Glass         | Na <sub>2</sub> O | MgO  | Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | P <sub>2</sub> O <sub>5</sub> | K <sub>2</sub> O | CaO   | TiO <sub>2</sub> | FeO  | CuO  | SnO <sub>2</sub> | Total |
|---------------|-------------------|------|--------------------------------|------------------|-------------------------------|------------------|-------|------------------|------|------|------------------|-------|
| Bead<br><584> | 0.49              | 0.77 | 0.37                           | 69.79            | 0.33                          | 19.63            | 2.66  | bd               | 0.22 | 5.21 | 0.37             | 98.82 |
|               | 0.4               | 0.8  | 0.34                           | 69.7             | 0.31                          | 19.75            | 2.69  | bd               | 0.17 | 5.24 | 0.48             | 98.39 |
|               | 0.57              | 0.73 | 0.39                           | 69.58            | 0.37                          | 19.72            | 2.55  | bd               | 0.2  | 5.19 | 0.61             | 98.36 |
|               | 0.5               | 0.73 | 0.36                           | 70.21            | 0.24                          | 19.43            | 2.63  | bd               | 0.22 | 5.16 | 0.38             | 96.11 |
| CL324 anl     | bd                | bd   | 3.91                           | 48.15            | bd                            | 15.14            | 29.85 | 0.51             | bd   | 1.78 | bd               |       |
| CL324 rpd     | 0.1               | 0.05 | 3.8                            | 48.7             | -                             | 14.6             | 30.1  | 0.5              | 0.04 | 1.8  | -                |       |
| CL330 anl     | 9.67              | 6.58 | 4.28                           | 54.82            | bd                            | 1.68             | 22.32 | bd               | 0.22 | bd   | bd               |       |
| CL330 rpd     | 9.5               | 6.6  | 4.3                            | 55.4             | -                             | 1.5              | 21.9  | -                | 0.27 | -    | -                |       |

A total of two additional beads were selected by the archaeological team for non-destructive analysis by X-ray fluorescence spectrometry (XRF) without sampling; these were small find 568 (the decorated bead) and small find 575 (a better preserved plain annular bead). The XRF results, however, are only used qualitatively because the surface of the beads is very likely to be chemically altered by weathering, the cremation temperatures, and adhering material. The XRF is an EDAX Eagle, which targets an area approximately 0.5 mm diameter, with a voltage of 40 kV. The XRF was also used to investigate the opacifiers in the decorated bead and to seek particular elements, such as antimony, which the XRF is better able to detect if it is present in small amounts.

## 2.2. Preparation of Experimental Melts

To investigate chlorine solubility and final glass melting temperature, an experimental glass batch was created to replicate mixed-alkali LMHK glasses containing both sodium and potassium oxides in fairly equal amounts, which is the most common composition found. Laboratory reagents were used instead of refined plant ashes and some of the sodium was added as sodium chloride. The batch composition was 3.6 g  $\text{CaCO}_3$ , 75 g  $\text{SiO}_2$ , 2 g  $\text{NaCl}$ , 12.3 g  $\text{Na}_2\text{CO}_3$ , 4 g  $\text{Cu}_2\text{O}$ , and 14.7 g  $\text{K}_2\text{CO}_3$ , and the batch was fired in a crucible at 1100 °C. A second melt was also prepared containing more copper oxide (8 g).

## 3. Results

### 3.1. Composition of the Bronze Age Beads

#### 3.1.1. The Transparent Blue Glass

Table 1 gives four SEM-EDS analyses of different areas of the sample from annular transparent blue Stotfold bead <584>. The glass contains high levels of potassium oxide and very little calcium and magnesium oxide or chlorine. These characteristics are unique to the LMHK glass type, which has been found at other European Late Bronze Age sites [6,8].

The transparent blue glass was coloured by copper oxide and was homogenous throughout, apart from occasional particles of tin oxide surrounded by potassium tin silicate crystalline reaction products. Analysis of these tin oxide particles detected low levels of copper as well, but no other metals. The tin oxide is likely to have entered the glass as an unintentional addition with the copper-based colourant, for example oxidised scale from bronze metal, or dross, from bronze alloy working. The copper oxide has dissolved readily in the glass, so now only the poorly soluble tin oxide particles remain. The use of copper oxide colourant containing traces of tin oxide is a common characteristic of contemporary Bronze Age glass [6].

However, there are some differences between the compositions of the Stotfold bead and other published examples of LMHK glass, in particular the low alumina and iron contents, and the atypically high ratio of potassium to sodium oxides (Figure 2a,b); most LMHK glass contains several weight percent of sodium oxide in addition to potassium. These differences are explored further below.

#### 3.1.2. The Opaque Glass Stripes

Non-destructive XRF analysis was used to investigate the composition of the surface of cylindrical decorated bead small find 568 as well as one other better-preserved plain bead small find 575. The analysis was of weathered surfaces, and so was qualitative, but it demonstrates that the same type of LMHK glass was used (Figure 3). Visually, the blue transparent glass core of the decorated bead <568> was very similar to the accompanying plain examples. Potassium, silicon, and copper were detected in the decorative opaque trails, with low levels of aluminium and calcium, and traces of tin; therefore, the glass used for the trail was again the LMHK type, similar to annular bead <584>. The presence of copper and tin oxides may indicate that the greyish-white opaque stripes were made by opacifying the same transparent blue glass. However, this cannot be determined with certainty, because the white glass is applied thinly over the blue glass body, and therefore some X-rays may be detected from the blue glass beneath the white trail, even when only the white trail is targeted. Antimony oxide, which was commonly used to make ancient glass opaque, was not detected. Low amounts of tin oxide, also used as an opacifier at certain times, were present, but these matched the levels found in the transparent core of bead <568>, as well as in the accompanying plain beads (see above); therefore, it is present as an unintentional contamination and is not responsible for the whitish-colour of the trails.

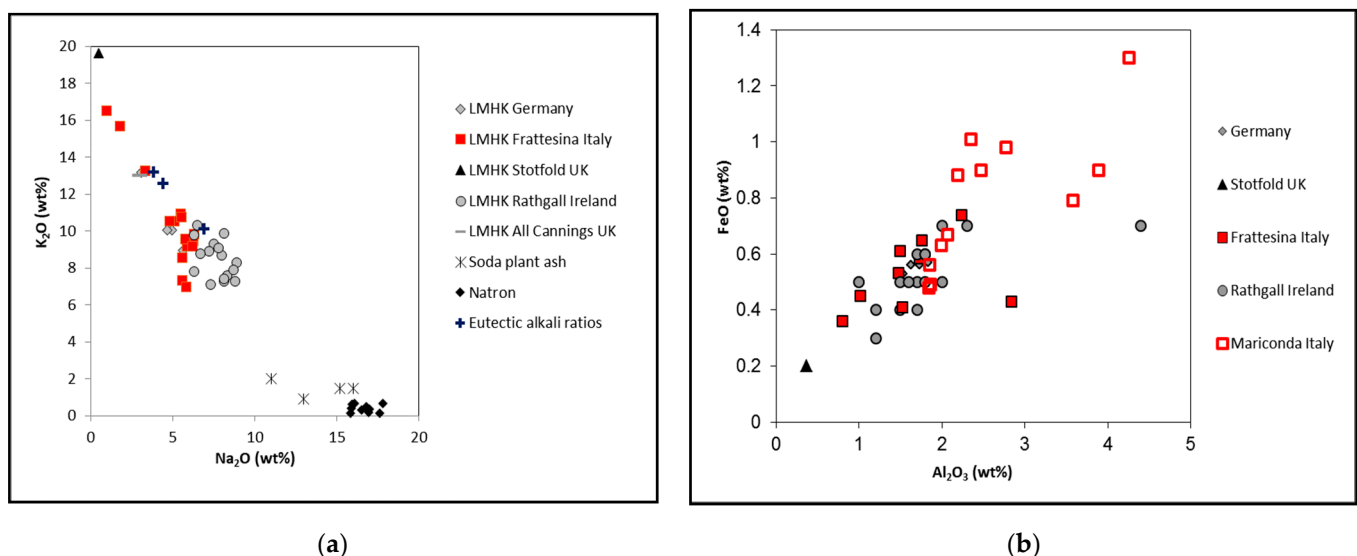
Several innovative methods were used in the Bronze Age for making glass opaque without the use of tin or antimony oxides. For example, some white Bronze Age beads found in Italy contain more calcium than contemporary beads of other colours [8] and other beads are opacified by recrystallised silica from added quartz [11]. As the ratio of calcium to potassium in Stotfold bead <568> was similar for both the blue transparent core

and opaque trail, it is more probable that silica accounts for the opacity of the pale glass trails decorating the surface. This additive would also raise the viscosity of the glass at a given temperature, contributing to the bubbly, pitted texture and raised profile of the opaque trails. The optical properties of silica crystals and bubbles make them less effective as opacifiers in silicate glasses, and the stripes have a greyish tone instead of the uniform, crisp white that would be produced by antimony or tin oxides [17].

### 3.1.3. A Comparison with Other LMHK Glass Beads in Europe

LMHK glass has been identified in Ireland at Rathgall (revised to 1150–1000 BC) and at sites across Europe, including Hauterive-Champréveyres in Switzerland (11th century BC), at Frattesina in Italy (11th to 10th centuries BC), and at a number of Bronze Age sites in France and the Northern Hessian area of Germany [6,11,18]. LMHK glass was used for a variety of colours but translucent turquoise blue was by far the most common. The concentration of material in the region and the evidence of production at Frattesina indicate that this glass is a European product. There are potentially other production sites yet to be identified, as some LMHK glass finds pre-date Frattesina [11] and researchers have also highlighted possible typological groupings that may suggest different production sites [8]. The date of the Stotfold cremation, and by association the Stotfold beads, is broadly contemporary within the context of these widespread European finds.

The Stotfold beads share the distinctive chemical characteristics of contemporary LMHK glass beads, in particular the low chlorine, calcium, and magnesium oxide contents (Table 1), the overall levels of combined alkali fluxes, the high ratio of potassium to sodium oxide (Figure 2a), and the use of copper oxide (with small amounts of tin oxide) as a colourant. This combination of attributes is unique to the LMHK group. The composition of the Stotfold bead is slightly atypical though; it contains less sodium oxide and more potassium oxide than other reported LMHK analyses (20 wt% potassium oxide as opposed to around 11 wt %) (Figure 2a). The alumina and iron levels in the glass are also low (Figure 2b) although correlated with other LMHK glasses. It is likely that a source of silica from the purer end of the range available, whether quartz sand or even crushed quartz pebbles, was used to make this glass.

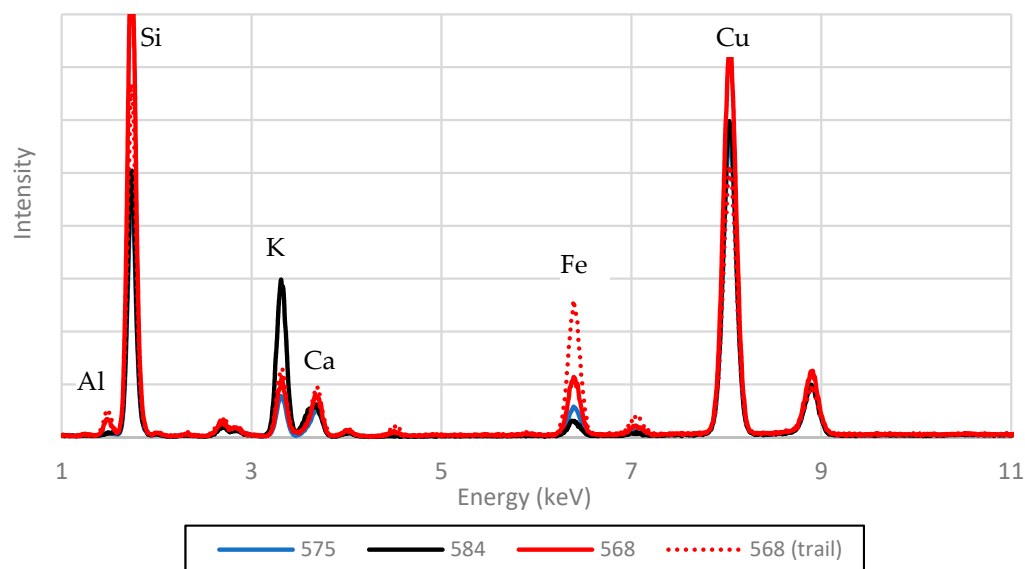


**Figure 2.** (a) Plot of alkalis (sodium versus potassium oxides) for Bronze Age LMHK glass, showing a consistent ratio, are different to natron and soda plant ash glass; (b) Ratio of iron to alumina oxides in LMHK glass from different European sites showing a consistent ratio (data from [11,18]).

The differences in LMHK glass compositions may be simply due to the inherent variability of LMHK glass, because of inconsistencies in raw materials and firing temperatures



or times (see later), and a small number of samples from Frattesina also contain in excess of 13 wt% potassium oxide [8–10]. Prolonged firing in a wood-fired furnace (or possibly the cremation pyre in this case), can increase the potassium oxide content of glassy materials because the burning fuel releases fumes rich in potassium oxide [19]. Cremation temperatures can also deplete the glass surface of sodium oxide [16]. Alternatively, the different types of LMHK glass composition may have been made in different places or at different times, and this may become more apparent as more examples are found and analysed. Henderson et al. have proposed that LMHK glass with a higher potassium oxide originated from near Rome (based on isotope studies) whereas the mixed-alkali LMHK glass (containing both sodium and potassium) was made from more local material in the Po valley, and that the two may have been mixed to make some of the glass at Frattesina [20].



**Figure 3.** Comparison of XRF spectra of beads SF575, SF584, and SF568 showing their very similar chemical composition, dominated by potassium, silicon, and copper oxides. The white trail on SF568 contains slightly higher relative iron, aluminium, and calcium oxides, however there was more soil adhering to SF568 because of its porous surface.

### 3.2. Experimental Recreation of the Glass

The possible source of the alkalis, sodium, and potassium oxide in LMHK glass has been a point of interest for researchers, and a wide range of possible alkali sources have been investigated, from natron to efflorescent salts from latrines or manurial soils [8,12,18,20,21]. The ashes of plants are considered the most likely candidate, as they contain both sodium and potassium salts in varying proportions, with the ratio depending on the species of plant, the geology where the plant grew, the part of the plant burnt, and the temperature attained [14,22,23]. Halophytic (salt tolerant) plants from desert, coastal, or marsh environments tend to produce ashes rich in sodium and chlorine whereas plants such as bracken or hard wood species produce ashes containing more potassium and little chlorine; interestingly, dung has been found to produce ashes containing both sodium and potassium alkalis in comparable ratios to LMHK glass [24–28]. The composition of the ashes and the glass potentially made from them must be compared with caution however, because not all of compounds present in the ash will react or be incorporated into the resulting glass due to their limited solubility in the glass melt [29] (and see later).

Assuming that LMHK glass was made using complex ashes containing both sodium and potassium salts, such as from halophytic plants or dung, then these must have been processed in some way to separate the alkalis from the majority of the other components present, including lime, magnesia, and phosphorus [14,30]. This could be achieved by making a solution with the plant ashes, straining out the insoluble portion of the ash,

then precipitating the alkali salts from the solution, or efflorescing the alkali salts. Many authors have concluded that plant ashes purified in this way were used to make LMHK glass [18,21]. This was a technique that was also practiced by Venetian glassmakers in the medieval period; medieval documentary accounts describe how plant ashes were heated in water, dissolving the sodium and potassium salts, the residue was filtered off, and then the alkalis were re-precipitated from the solution [31].

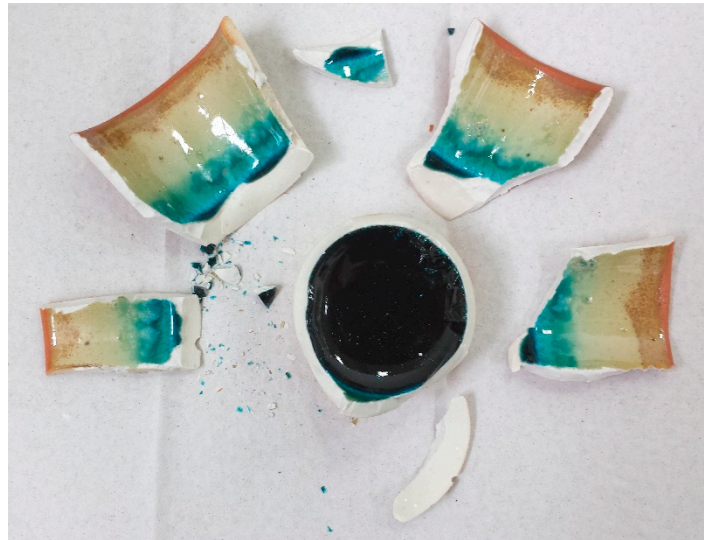
Sodium chloride, being soluble, would be retained even in purified salts however, whereas LMHK glass typically contains less than 0.1 wt% chlorine regardless of the sodium content [18]. This is difficult to explain because chlorine is consistently present in the potential alkali sources for these ancient glasses, including refined sodium-bearing plant ashes, natron, and any efflorescent salts and precipitates from various alkali salt solutions. Consequently, virtually all ancient glass containing sodium oxide as a flux also contains some chlorine; this includes glass made from soda-rich plant ashes or natron, which contains about 1 wt% chlorine. However, the solubility of chlorine in silicate melts is influenced by the glass composition and temperature [32]. The low chlorine content of LMHK suggests that less chlorine was present, that it was less soluble in this composition of glass, or a combination thereof, either because of the unusual composition of LMHK glass or because of the processes and temperatures used in production; these potential factors are explored in the following sections.

### 3.2.1. Single-Stage Batch Melting

To investigate chlorine solubility and final glass melting temperature, an experimental glass batch was created to replicate mixed-alkali LMHK glasses containing both sodium and potassium oxides in fairly equal amounts, which is the most common composition found (the Stotfold beads are from the high potassium end of the range but this is atypical). The details are given in Section 2.2 and Table 2 (the predicted composition of the first batch is Predicted 1 and the second batch Predicted 2). The first batch did not fully melt at this temperature, but a second melt (Table 2, Predicted 2) containing more copper oxide (8 g) produced a homogenous blue glass (Figure 4). The composition, confirmed by SEM, included dissolved chlorine at higher levels (0.7 wt%) than those found in the archaeological material (less than 0.1 wt%) (Table 2). The archaeological glasses also have slightly more complex compositions (with small amounts of aluminium, magnesium, phosphorus, and iron oxides), which probably help to reduce the melting temperature slightly compared to this experimental glass. Nonetheless, this experiment demonstrates that high temperatures of 1000 °C, possibly more, are needed to melt the LMHK composition and that chlorine is soluble in LMHK glass at these temperatures. It is therefore unlikely that mixed-alkali LMHK glass was made in a single melting stage, directly combining purified alkali salts, a silica source, and colourant, because some chlorine would have been carried through and then dissolved in the glass.

**Table 2.** Simplified composition of experimental sodium- and potassium-rich LMHK glass made from laboratory reagents, melted at 1100 °C, analysed by SEM-EDS (average of 3), bd = below detection, normalised (av. total 97.0 wt%).

| Batch       | Na <sub>2</sub> O | SiO <sub>2</sub> | Cl  | K <sub>2</sub> O | CaO | CuO |
|-------------|-------------------|------------------|-----|------------------|-----|-----|
| Predicted 1 | 8.8               | 73.8             | 1.2 | 9.9              | 2   | 4.4 |
| Predicted 2 | 8.4               | 70.7             | 1.1 | 9.4              | 1.9 | 8.4 |
| Measured 2  | 7                 | 73.9             | 0.7 | 7.5              | 1.9 | 8.9 |



**Figure 4.** Blue experimental melt in a broken crucible, made from laboratory reagents mimicking the production of LMHK glass from refined, sodium-, and potassium-rich plant ashes (Table 2), melted at 1100 °C.

### 3.2.2. Multi-Stage Production

The other option explored here is that the glass was made in a multi-stage process using one or more initial low temperature fritting steps, followed by a high temperature melting and homogenising stage. The lowest temperature at which a melt will form, and the composition of the melt, can be approximated from the  $\text{Na}_2\text{O}$ - $\text{K}_2\text{O}$ - $\text{SiO}_2$  ternary phase diagram. Although phase diagrams represent a system at equilibrium, which is rarely the case in practice, they are nonetheless useful for understanding reactions in archaeological glasses [33]. For the sodium, potassium, and silicon oxide system, there are three eutectic compositions where glass will form at under 700 °C, shown in Table 3 [34,35]. An initial fritting stage could therefore have taken place in a hearth fire, which can achieve 700 °C, and still produce a eutectic glass composition. The frit produced by heating a mixture of alkali salts and sand would comprise partially dissolved quartz grains in a glassy matrix. The frit could then be combined with additional quartz and some copper colourant and the batch heated in a final melting stage, dissolving the last of the quartz to form a homogenous glass. This final melting of the batch would require high temperatures, nearer to 1000 °C, and would require a specialised furnace.

**Table 3.** (Top) The low temperature eutectic compositions (wt%) for the  $\text{Na}_2\text{O}$ - $\text{K}_2\text{O}$ - $\text{SiO}_2$  system [34], and (bottom) the predicted composition of a final glass made by combining a frit with these eutectic compositions with quartz and colourant and homogenising at high temperature (see text and Figure 2a).

| Frit Glass                | Temp °C | $\text{Na}_2\text{O}$ | $\text{K}_2\text{O}$ | $\text{SiO}_2$                | $\text{K}_2\text{O}/\text{Na}_2\text{O}$ | $\text{Na}_2\text{O} + \text{K}_2\text{O}$ |
|---------------------------|---------|-----------------------|----------------------|-------------------------------|--|--|
| Eutectic a                | 540     | 8                     | 23                   | 69                            | 2.9                                      |  |
| Eutectic b                | 645     | 11.7                  | 40.1                 | 48.2                          | 3.4                                      |  |
| Eutectic c                | 665     | 17.2                  | 25.4                 | 57.4                          | 1.5                                      |  |
| Final Glass               | Temp °C | $\text{Na}_2\text{O}$ | $\text{K}_2\text{O}$ | $\text{SiO}_2 + \text{rdr}^1$ | $\text{K}_2\text{O}/\text{Na}_2\text{O}$ | $\text{Na}_2\text{O} + \text{K}_2\text{O}$ |
| Frit a + rdr <sup>1</sup> | ~1000   | 4.4                   | 12.6                 | 83                            | 2.9                                      | 17   |
| Frit b + rdr <sup>1</sup> | ~1000   | 3.8                   | 13.2                 | 83                            | 3.4                                      | 17   |
| Frit c + rdr <sup>1</sup> | ~1000   | 6.9                   | 10.1                 | 83                            | 1.5                                      | 17   |

<sup>1</sup> rdr = remainder of components of batch including  $\text{SiO}_2$  and CuO, etc.



Comparing archaeological LMHK glass with theoretical glasses derived from the three lowest temperature eutectic compositions for the  $\text{Na}_2\text{O}$ - $\text{K}_2\text{O}$ - $\text{SiO}_2$  system provides strong support for this multi-stage model of glass production (Table 3). In low temperature fritting, the proportions of potassium oxide to sodium oxide in the glassy areas that form should move towards these eutectic compositions, regardless of the proportions of the alkalis present in the original mixture. The ratio of potassium to sodium oxides will stay relatively unchanged through to the final glass, unaffected by the later addition of more quartz and the colourant. In Table 3, the eutectic compositions are shown, as well as the theoretical compositions of glasses made from each of these frits, maintaining the ratio of potassium to sodium oxides, and resulting in glasses with a total alkali content of 17 wt% to best match archaeological examples. The compositions of these theoretical glasses have been plotted against the archaeological examples in Figure 2a. The theoretical glass composition based on the lowest eutectic is an excellent match for the majority of LMHK glass artefacts, and the remaining, more potassium-rich, archaeological compositions cluster with the two slightly higher temperature eutectic compositions. This suggests a simple explanation for the spread in composition of the archaeological glasses; it is most likely due to slight variation in the first stage fritting temperature used by the glassmakers, with occasional higher fritting temperatures resulting in a final glass with a higher ratio of potassium to sodium oxides.

### 3.2.3. Experimental Summary

In summary, LMHK glass requires homogenising at temperatures of around 1000 °C to make a glass but it is unlikely that it was produced in a single batch firing; instead, a multi-stage process was probably used. A low temperature (around 700 °C) fritting process in a hearth can account for some of the unusual compositional characteristics of mixed-alkali LMHK glass, in particular the ratio of potassium to sodium oxides and the spread in this ratio. The alkalis may have been concentrated beforehand, from the ashes of halophytic plants or dung, by dissolving, filtering, and precipitating, or by efflorescing, the salts. This was followed by low temperature fritting of quartz sand with the alkalis to produce a frit comprising quartz grains coated with eutectic composition glass. A final high temperature firing in a specialized furnace would be needed to dissolve the last of the quartz and homogenise the glass, with the colourant added in this step if not before. Angelini et al. estimated the melting temperature of LMHK glass at 900 °C to 1000 °C [10].

The low chlorine content of LMHK glass, despite the presence of sodium in the composition, demands further investigation. Because chlorine solubility is affected by both composition and temperature, it may be that the use of low temperature fritting stages leads to less chlorine being dissolved into the glass from the raw materials than would be incorporated through single stage, high temperature batch melting; however, this hypothesis requires experimental testing.

## 4. Discussion

In the medieval period, glassmakers used purified ashes because they wanted to make colourless glass, however, the makers of LMHK glass were making strongly coloured glass for the most part, so this was not their main motivation; instead they were finding methods for reducing the melting temperature of their glass with the fluxing materials available to them. Untreated plant ashes originally contain a high proportion of calcium and magnesium compounds relative to alkalis. Although untreated ashes could be combined with sand or quartz pebbles to make a glass, as was the case in much of Europe in the medieval and post-medieval periods, the temperature required to melt the mix could be as much as 1300 °C and heavily dependent on the proportion of alkali in the ash [36]. By purifying the plant ashes and using a multi-stage process to further concentrate the alkalis, the glassmakers would have been able to reduce the melting and working temperature of their glass substantially. The high concentration of copper oxide colourant (5 wt%) appears

to have stabilised the glass in the absence of calcium or magnesium oxides, and also acted as an additional flux.

#### *Multi-Stage Glassmaking and Faience*

The origins of the proposed complex multi-stage glassmaking process might be found in the closely related faience industry. Faience comprises quartz particles sintered together by areas of glass, with an overall glazed surface [10,21]. Bronze Age faience artefacts made in Italy have been found to have LMHK composition glazes, suggesting a possible link with LMHK glass. Faience can be made by direct application of a glaze mixture to the object, by cementation, or by efflorescence, or some adaptation of these [25,37]. Santopadre and Verità have suggested, based on the composition and microstructure of LMHK faience and the homogeneity of the glass within it, that it was made from a prior frit material. They explored whether the frit was made by heating quartz in a cementation glazing powder to form a low temperature potassium-sodium glass around the quartz particles, and that this was then mixed with water and more quartz and re-fired to make glassy LMHK faience. Experimental work with cementation glazing has since demonstrated that cementation typically introduces some calcium and chlorine to the glaze [25,38], although this is temperature dependent, so the precise details of the faience multi-stage model require more investigation. Nonetheless, the proposed first fritting step for making LMHK faience has many parallels with the process suggested here for LMHK glassmaking, and the acquired experience and observations from faience-making could have been adapted for glassmaking, with similar materials and methods.

## 5. Conclusions

Analysis of the Stotfold beads found that they are made from low magnesium, high potassium (LMHK) glass. This type of glass was prevalent in Europe from about 1200–900 BC, confirming the association between the Stotfold glass beads and the cremated bone (dating to the Later Bronze Age) with which they were found. Although glass beads with this general composition are known from sites in Ireland, the Stotfold beads are only the second example of this glass type identified in England and appear to pre-date other examples from the UK. As they were made in continental Europe, they represent evidence of exchange with, or even travel between, distant communities, and their rarity testifies to the high status of the individual whose remains were interred with beads. For the Stotfold beads, the glassmakers relied on quartz grains to make the opaque glass for decorating the beads rather than tin or antimony opacifiers.

The glassmakers were skilled in their selection and preparation of their raw materials, seeking a clean source of silica. They may have concentrated alkali salts from plant or dung ashes to make the glass. The glassmakers probably used a low temperature fritting stage (~700 °C), heating a combination of quartz or sand with the alkali salts in a hearth. The resulting frit comprised undissolved quartz and interstitial mixed-alkali glass. A final high temperature melting and homogenising stage was used to produce the final glass. As a result, the ratios of potassium to sodium oxides in LMHK glass artefacts matches low temperature eutectic glass compositions. The unexpectedly low chlorine content of LMHK glass may also be a result of multistage production, but this aspect requires experimental investigation.

This complex glassmaking process may have developed from the established practice of faience-making in the region and allowed the production of a glass that would melt and could be worked at achievable temperatures, which would not have been possible with the same type of plant ashes if used directly and in an untreated state.

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