**The use of Electron Probe Microanalysis and Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry for the investigation of 8th-14th century plant ash glasses from the Middle East** 

# **Julian Hendersona1 , Simon Chenerya,b , Edward Faber<sup>a</sup> and Jens Kröger<sup>c</sup>**

<sup>a</sup>Department of Archaeology, School of Humanities, University of Nottingham, University Park, Nottingham, NG7 2RD, U.K, (julian.henderson@nottingham.ac.uk); <sup>b</sup>British Geological Survey, Keyworth, Nottinghamshire, NG12 5GG, U.K, (srch@bgs.ac.uk); Geschwister-Scholl-Str. 6, 10117 Berlin, Germany, (jens.sasan.kroeger@gmx.net)

### **Abstract**

This is the first broad survey using major, minor and trace element analysis of 8th-15th AD plant ash glass from the Middle East across a 2000 mile area stretching from Egypt to northern Iran. This was part of the ancient Silk Road that extended from the Middle East, through central Asia to China. Up to now, some compositional distinctions have been identified for such glasses mainly using major and minor element oxides and radiogenic isotopes. Our new trace element characterisation is for glass found in selected cosmopolitan hubs, including one where there is archaeological evidence for primary glass making. It provides not only far clearer provenance definitions for regional centres of production, in the Levant, northern Syria and in Iraq and Iran, but also for sub-regional zones of production. This fingerprinting is provided by trace elements associated with the primary glass making raw materials used: ashed halophytic plants and sands. Even more surprising is a correlation between some of the sub-regional production hubs and the types of glass vessels with diagnostic decoration apparently manufactured in or near the cosmopolitan hubs where the glass was found such as colourless cut and engraved vessels (in Iraq and Iran) and trail-decorated vessels (in the Levant). This therefore provides evidence for centres of specialisation. Our trace element characterisation provides a new way of defining the Silk Road by characterising the glass that was traded or exchanged along it. Taken together this data provides a new decentralised model for ancient glass production.

### **Key words**

<sup>&</sup>lt;sup>1</sup> Corresponding author. Telephone number 0044-115-951-4849. Email: julian.henderson@nottingham.ac.uk.

Glass technology, trace element analysis, provenance,

## **1. Introduction**

The existence of the Silk Road between the Middle East and China is reflected in the occurrence of a wide range of materials including silk, glass, metals and ceramics particularly found in cosmopolitan hubs. Part of its existence is recognisable from as early as the 4th century BC. Materials may have moved in a range of ways including trade and the resulting distributions are more analogous to a modern day "virtual network" than to a physical road. A peak period of interaction was between the 6th and 9th centuries AD when the Tang Dynasty Chinese and (from 750 AD) the Abbasid caliphate were at political and economic peaks. Between the Mediterranean basin and ancient Persia there were a number of multi-ethnic hubs including Cairo, Damascus, Beirut, Al-Raqqa, Ctesiphon, Samarra and Nishapur. Some of these hubs would have had extensive industrial complexes where glass was fused from raw materials. Either raw glass or the vessels made from it would have been fed into the exchange and trade networks on the land-based Silk Road and the connected water-borne Silk Road, both ultimately leading to south-east Asia.

A range of glass vessel types with characteristic decoration were made between the 8th and 15th centuries [1]. Some of these, including lustre-decorated, scratch-decorated, cameo-decorated, colourless cut and engraved vessels, have been found along the Silk Road as far away as China [2]. One of the best collections of typical west Asia vessels has been found on the famous 9th century Famen temple site in Shaanxi province, northwestern China.

Ancient glass technologies changed over time in the Middle East. The earliest glass (from c. 2400-c. 1000 BC) was made from ashed halophytic plant ashes and crushed quartz or sand (referred to here as plant ash glass [PAG]). Between c. 1000 BC and 800 AD this was followed by the use of an evaporitic alkaline salt, natron, combined with sand. After this date PAG was reintroduced and

continued to be used (albeit with other glass compositional types) until c. 17th century AD. Some PAGs dating to between c. 1000 BC and 800 AD have been found, with the Sasanians (3rd to 7th centuries AD), in particular, using the technology, but the Hellenistic Greeks, the Romans, the Byzantines and cultures of early medieval Europe mainly used natron glass.

Scientific research on ancient glass has provided evidence for changing technologies over time and for broad (and sometimes somewhat narrower) geographically defined production zones [3-8]. Analysis of glass using especially Sr and Nd [and B] isotopes has sometimes led to better defined production zones based on a geological provenance [9-11]. Historical references to glass manufacture can provide indications about production [4, 12] and possible broad production zones based on decorative styles and production techniques for Islamic vessels have been suggested on archaeological and art historical grounds [13-15].

Here we present new scientific analyses and interpretation from electron probe microanalysis (EPMA) and laser ablation inductively coupled plasma mass spectrometry (LAICPMS) for glass deriving from the urban centres in an area between Egypt and northern Iran. These centres are 9th century Beirut (the Lebanon), 11th-12th century Damascus (Syria), 9th century Al-Raqqa (Syria), 9th century Samarra (Iraq), 9th-10th century Ctesiphon -Islamic al-Madā'in (Iraq), 9th-10th century Nishapur (Iran) and 14th-15th century Cairo (Egypt). We have also included samples of glass from a late phase (8th-10th century) of the important palatial site of Khirbat al-Minya (Israel). Until now, scientific analysis of Middle Eastern Islamic plant ash glass vessels has largely been the determination of major and minor elements and isotopes [16-20], but not to large-scale trace element analysis or the study of glasses deriving from sites across a broad geographical area.

The main objectives of this work are first to investigate whether variations in the chemical compositions of the glasses form groups that can be correlated to the zones in which they were found or made. A second objective is to assess whether chemical variations in the glasses can be correlated with specific vessel decorative types and/or colours.

## **2. Methodology**

### *2.1 Materials*

This article focuses on glasses found on the sites listed above. A list of samples is given in Table 1 where the sample number, the site, vessel type and colour is provided. Samples of a range of vessel types and decorations have been analysed so as to investigate any possible links between, their chemical compositions and the locations in which they were found, vessel types and decorations. The vessel types sampled include some that are typical for the period. They include colourless cut and ground vessels mainly found on sites in Iran and Iraq (Nishapur, Samarra and Ctesiphon), vessels with applied decorative strings with green bodies (Nishapur), colourless pinched decorated vessels (Nishapur and Samarra), scratch decorated vessels (Samarra), cameo decorated (Samarra) and enamelled mosque lamps bearing dedications to specific emirs based in Cairo whose reigns are given in Table 1. Although the mosque lamp samples are 200-400 years later than the rest, there is an overall coherence in the results. Undecorated vessels samples analysed include beakers, vases, bottles, bowls, phials, flasks and grenades from Ctesiphon, Beirut, Damascus, Khirbat al-Minya and Al-Raqqa. We have also analysed samples of coloured wall plates from Samarra and window glass from Khirbat al-Minya and Al-Raqqa for comparison. Samples from the only archaeologically proven primary glass making site, where glass furnaces were excavated, are those from Al-Raqqa. We have included samples of raw furnaces glasses of a range of colours. We were careful to make sure that the samples did not derive from a zone of interaction with the furnace floor. Photographs of representative samples are given in Figure 1. The glass samples from Ctesiphon, Khirbat al-Minya, Nishapur and Samarra were taken from vessels housed in the Museum for Islamic Art in Berlin, Germany; the samples from Beirut, the Lebanon derived from excavations directed by Dr Hans Curvers; those from Damascus, Syria derived from the citadel excavations directed by Dr Sophie Bertier; those from Al-Raqqa, Syria from excavations of the industrial complex there directed by the first author; the mosque lamps are housed in the Museum of Islamic Art, Doha, Qatar. The locations where the glass was found are given in Figure 2: it was found in an area covering a distance of some 2000 miles between the Levant and northern Iran.



(a) Facet cut bowl fragments from Ctesiphon in Iraq (b) Undecorated flask from Khirbat (samples CTES 15 and 16)

al-Minya in Israel (sample KAM 11)



(c) Pinch decorated beaker and trail decorated (d) Pinched and scratch decorated bowl rim fragments from Nishapur, Iran (samples NISH 9 fragments from Samarra, Iraq (samples SAM and 17) 11 and 15)





(e) A cameo decorated bowl fragment and a wall plate (f) A small fragment of glass furnace floor from Samarra, Iraq (samples SAM 17 and 35) from Al-Raqqa, Syria with raw purple glass



 attached (sample RAQ 38). Hundreds of other fragments were found there

**Figure 1 Photographs of representative fragments of glass from which samples were removed**  (photographs: J. Henderson)



**Fig 2**

# **Table 1 List of samples**

NISH= Nishapur, SAM= Samarra, CTES= Ctesiphon, BEI= Beirut, DAM= Damascus, KAM= Khirbat al-Minya, RAQ= Al-Raqqa (Raqqa TZ= Tell Zujaj, Raqqa. Raqqa sample numbers: first number refers to samples in [21], second, in brackets, refer to sample numbers used in publication of electron microprobe data in [18]; \*= suggested production centre (mosque lamps dedicated to emirs based in Cairo).









### *2.2 Methods*

#### **Electron probe microanalysis**

Electron probe microanalysis is one of the most accurate techniques for the analysis of silicates [23]. The analysis of 1-2mm samples was performed using EPMA-WDS using a JEOL JXA-8200 electron microprobe in the Department of Archaeology, University of Nottingham as described elsewhere [24]. A defocused 50μm electron beam was used. Twenty six elements were sought, presented as oxide weight percentage: 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>, SO<sub>3</sub>, Cl, K<sub>2</sub>O, CaO, TiO<sub>2</sub>, V<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, MnO, FeO, CoO, NiO, CuO, ZnO, As<sub>2</sub>O<sub>5</sub>, SrO, ZrO<sub>2</sub>, Ag<sub>2</sub>O, SnO<sub>2</sub>, Sb<sub>2</sub>O<sub>5</sub>, BaO and PbO. Three areas of interest at ×1000 were analysed for the main glass phase of each sample and the results were averaged. Quantification of detected oxides was performed with a PRZ correction routine. The following relative analytical accuracies were obtained using the Corning B standard as unknown:  $3\%$  for Na<sub>2</sub>O; 2.5% for  $SiO<sub>2</sub>$ ; 1.5% for K<sub>2</sub>O; 1.5% for CaO and 2% for PbO. For minor elements the accuracy was 5% for MgO, 2.5% for Al<sub>2</sub>O<sub>3</sub>, 15.5% for P<sub>2</sub>O<sub>5</sub>, 6.5% for FeO, 5% CuO and up to 13% for Cl. A fuller consideration of analytical errors in the EPMA analyses of ancient glasses is published elsewhere [24]. The following elements were sought but not detected: V, Cr, Ni, Ba, Sn, Zn, Sr, Ag, As, Zr. Table 2 provides a comparison between the quoted and measured values for detected oxides in the Corning B glass standard, with associated standard deviations.

Table 2: The recommended composition for the Corning B standard [25] compared to average analytical results (n=20) and associated standard deviations using the electron microprobe.



Note: \* FeO composition for Corning B calculated from published value for  $Fe<sub>2</sub>O<sub>3</sub>$ 

### **Laser ablation inductively coupled plasma mass spectrometry**

The use of LA-ICP-MS for the trace element analysis of glass is a now widely accepted practice, even within the naturally conservative forensic community [26].

Trace element determinations were carried out using by laser ablation-inductively coupled plasma mass spectrometry (LAICP-MS). The same samples were used as for EPMA. Prior to analysis the samples were cleaned by rubbing a tissue soaked in dilute acid over the surface for a few seconds. The laser ablation unit was a NewWave (Electro Scientific Industries, Inc.) UP193 nm excimer system. The sample was placed in a simple single volume ablation cell with a 0.8 Lmin<sup>-1</sup> He flow. In addition to the sample block NIST glass standards SRM610 and 612 were placed in the chamber. The laser was normally fired at 5 Hz for 60s using a beam diameter of 70 um. Fluence and irradiance as measured by the internal monitor were typically 3 J/cm<sup>2</sup> and 0.85 GW/cm<sup>2</sup> respectively. Prior to introduction into the ICP-MS the He flow was mixed, via a Y-junction, with a 0.85 Lmin<sup>-1</sup>Ar and 0.04 Lmin<sup>-1</sup> N2 gas flows supplied by a Cetac Aridus desolvating nebuliser. The Aridus allowed introduction of ICP-MS tuning solutions and optimisation of the Aridus sweep gas (nominal 4Lmin<sup>-1</sup>Ar). During solids analysis by the laser, the Aridus only aspirated air. The ICP-MS used in this study was an Agilent 7500cs series instrument. The instrument was set for 100 sweeps of the 47 isotopes of interest per integration. The dwell time for each isotope was 1 ms giving an integration time of 5s. Data were collected in a continuous time resolved analysis (TRA) fashion. Prior to laser firing a period of at least 120s of 'gas blank' were collected, then 3 ablations being made on the SRM610; 3 ablations on the SRM612; 3 ablations on up to 8 samples and a final 3 ablations on the SRM610. The SRM612 was used to calibrate the system whilst the SRM610 was used as a quality control (QC) material; aggregated results for each element-isotope concentration are given in Table 3. All calculations and data reduction were performed manually in Excel spreadsheets and statistical analysis using MiniTab v13. The nature of laser ablation means there is some variability in ablation volume and transport efficiency with different materials (matrix effects). Therefore, accepted practice is to normalise results to an internal standard element, in the current study Si was chosen for this purpose with its concentration being known in the NIST glasses and provided by the EPMA data for the study glasses.



**Sample: SRM610 Number of analyses=72 Number of analytical session = 5**





Appendix A provides a comparison between our LA-ICP-MS analysis of the Corning B standard, the expected composition [25] and Wagner et al.'s analytical assessment [27].Typical uncertainties (2s.e.m.) for sample analyses used in Figure 4-6 error bars were estimated using an analysis of variance (ANOVA) to separate the within-sample variance from the between sample variance. This ANOVA was based on the elemental concentration or ratio of the original 3 replicate ablation analyses for each of 10 colourless Nishapur glasses. The 3 replicates being combined into a mean for plotting in the Figures.

A number of bi-plots for both 2 sets of oxides and for ratios were created for both major/minor and trace element results, including for rare earth elements. Those provided here are considered to be the most instructive for the present study.

#### **3. Results**

Major, minor and trace element analysis has been carried out on 97 samples of plant ash glasses in order to examine relationships between glass compositions, dates, vessel types and provenance. Electron microprobe results are given in Appendix B and trace element results in Appendices C.1 to C.8. As noted above broad geographical provenances for Islamic plant ash glasses have been suggested before. The suggested areas have been 'Syria', 'Mesopotamia' and 'the Levant' mainly based on major and minor oxide concentrations such as sodium, calcium, magnesium, aluminium, iron and strontium [4], [17-19], [28].



### Figure 3

. This plot is provided so as to compare the electron microprobe results of glass samples that form the focus of this paper with other, mainly well dated, glasses mainly deriving from the same broad geographical area. In Figure 3 the glass samples that form the focus of this study have solid symbols (some additional 9th century Al-Raqqa furnace glass results have been plotted too); the balance of plotted data is represented by open symbols. Comparable furnace glass from a second (12th century) site in Al-Raqqa are plotted and results for raw glass from the Turkish early 11th century Serç Limani shipwreck and from the 8th-9th century Israeli secondary glass working site of Banias. Data for cut and ground colourless and coloured glass from (9th-10th century) Nishapur [16] and linear cut and facet cut colourless glass from the 9th-10th century Raya and Al Tur area, Egypt [19] are also included here for comparison. Two data sets for vessel body compositions of enamelled Ayyubid (11th century) and Mamluk (12th-14th century) vessels are presented here to provide a comparison with our results for the 14th-15th century enamelled mosque lamps [29-30]: they form a relatively coherent correlation defined by the parallel lines in Figure 3. The symbols used are intended to highlight a broad compositional trend that has been noted before [4]: glasses found and apparently made in Iraq and Iran (lozenges) have amongst the highest MgO levels and the lowest CaO levels; the furnace glasses from Al-Raqqa (triangles) fall between 'Levantine' glasses (circles) and the Iraqi/

Iranian glasses. The ratio of weight % MgO to CaO therefore changes according to the location moving from east to west. The compositional results for furnace glasses provide a degree of confidence for this interpretation because they have a fixed provenance but there are a number of instances where a provenance attribution is difficult to assign. Levantine and Iraqi/ Iranian glasses are well distinguishable from each other in the Figure 3 but it becomes more difficult to have confidence in the attribution of glasses plotting with Syrian furnace glasses. Examples are some Nishapur coloured glasses and the enamelled vessel samples. It is possible that some of these were made in other areas, such as Egypt.



## Fig 4

This is an important start but clearly the use of a more sensitive technique such as LA-ICP-MS for a wide range of elements is the next logical step. The data plotted in Figures 4-6 reflect the use of plant ashes and sands with varying geochemical characteristics to make the soda-lime-silica glasses. Figure 4, a plot of Cr versus Fe shows a clear distinction between glasses made in the Levant (including southern Syria) and Egypt on the one hand and northern Syrian/ Iraqi and Iranian glasses on the other; these trace elements are often associated with sand raw materials. With four exceptions, the eastern samples clearly have significantly more Cr for a given amount of Fe compared to the western samples. A cluster of seven Ctesiphon samples falls in the middle of the Fe concentration range. These are results for colourless or pale green facet cut vessels. Significantly, almost all AlRaqqa samples, including raw furnace glasses, fall on a linear correlation suggesting a dilution trend. When this plot is compared to slightly earlier Sasanian glasses [31-32] most have higher Cr and Fe with the majority having a higher proportion of Cr.

in a majority of cases have lower 1000Zr/Ti ratios [31-32].



## Fig 5

The issue of differential dilution of diagnostic contaminants by the silica component can be overcome by the use of ratio: ratio plots. In Figure 5 Levantine glasses tend to have lower Cr/La ratios than eastern glasses. The ellipses in Figures 5 (and 6) are provided as a visual means of emphasising the clustering of data from individual sites in the eastern zone. Amongst the eastern glasses in Figure 5 Nishapur samples are most like western ones, with Al-Raqqa mainly plotting at the 'interface' between Levantine and eastern samples. Most Ctesiphon samples separate into a group having the highest Cr/La ratio indicated by an ellipse. Some Samarra glasses have high 1000Zr/Ti and most plot in a negatively correlated field. Amongst Levantine glasses, those from Beirut can mainly be distinguished from Damascus glasses by their higher Cr/La and lower 1000Zr/ Ti ratios. Sasanian 4th-5th century plant ash glasses from Veh Ardašīr encompass the full range of Cr/La ratios found in our material but



### Fig 6

In Figure 6 some Levantine glasses have higher Cs/K ratios than Eastern glasses; conversely Eastern glasses tend to have higher Li/K ratios, particularly those from Nishapur and Samarra. Many Nishapur glasses are similar to Samarra glasses and four are more like Western material from the Levant. The Cairo samples have elevated Cs/K ratios and five form a cluster. Most Khirbat al-Minya glasses cluster together and can be distinguished from the mosque lamp glasses probably form Cairo and from glasses derived from Beirut and Damascus as indicated by ellipses). Although separable from other Levantine glasses Beirut and Damascus samples are indistinguishable in this plot (but are distinguishable in Fig 5). Surprisingly, the very low ratios found in a range of plant samples from Syria and the Lebanon [33] suggest that they cannot provide sufficient Cs or Li for the levels of K. This could therefore suggest that they may come in as a contaminant in the silica source.

For many glasses the Cr/La and Li/K values in Figures 5 and 6 respectively tend to increase moving from west (the Levant) to east (Iran and Iraq). These variations are ultimately determined by the geochemistry of the mountain ranges such as the Anti-Lebanon, Taurus, Zagros and Elburz from which the principle rivers such as the Barada, Euphrates and Tigris flow. The Nile in Egypt is a principle contributor to the geochemical characteristics of the southern part of the Levantine coast.

Conventional wisdom states that trace elements were introduced into the glass from either the silica sand source, as contaminant heavy minerals such zircon (Zr), rutile (Ti), illmenite (Ti), monazite (La), chromite (Cr), or from the plant ash source, as substitutes for K, Na (Li, Rb, Cs). However, this is likely to be an over-simplification since contamination of the silica sand source by alkali feldspars may bring in additional Li, Rb and Cs. Whilst significant La and Cr have been found in plant ashes [33], they may be associated with plant phytoliths; clay particles that have attached to poorly washed plants or sand may also provide a source of many elements including Zr, Ti, La and Cr.

Our results will now be discussed by sample origin moving from east to west, starting with Nishapur in north-east Iran and ending with Levantine sites. The results for Nishapur glasses plot mainly with other Eastern glasses, especially in Figures 4 and 6 and mainly with eastern glasses and northern Syrian glasses in Figure 5: a better discrimination for Nishapur glasses can be observed in Fig 6 where they plot almost exclusively within the ellipse containing only eastern glasses characterised by the highest Li/K ratios. Four of the samples tested plot with Levantine glasses in Figures 4, 5 and 6 (see section 4).

Eight of eleven Ctesiphon samples were taken from three 9th-10th century pale green and five colourless facet cut vessels. Nine samples fall into a well-defined eastern group with high Cr/La ratios in Figure 5. Seven of these are colourless or pale green facet cut vessels; the remaining 2 are a colourless bowl and an ovoid vessel. One colourless facet cut sample from Ctesiphon falls close to Al-Raqqa samples possibly indicating it was made in northern Syria; the second small pale green ovoid vessel sample plots amongst Samarra samples in Figure 5 so these vessels or the glass were probably imported to Ctesiphon.

Fourteen out of nineteen Samarra samples fall into a distinct negatively correlated group in Figure 5. These consist of four pale green mould-decorated vessels, five cameo decorated vessels, one pinchdecorated vessel, two scratch decorated vessels and two wall plaques (see Table 1). These results probably show that a range of characteristic early Islamic vessel types together with wall plaques were made in Samarra. Six Samarra samples with lower Cr/La ratios are separated from the main Samarra group in Figure 5. Intriguingly, unlike the correlated group, they all colourless, include cut

vessels and were made with sand containing low iron levels (see Figure 4). These glasses plot close together and are close to (amongst others) Nishapur colourless samples in Figure 5. These Samarra samples are far more clearly associated with those from Nishapur in Figure 6, confirming their eastern origin and were therefore probably imported to Samarra from Nishapur.

Al-Raqqa is located between the Levant and the Eastern zone of Iraq and Iran. Many Al-Raqqa samples also plot between Levantine and eastern glasses in Figure 5 and more clearly in Figure 6. The results include raw furnace glasses from the primary glass-making site at Al-Raqqa; these have more constrained Cr/La and Li/K signatures than detected in scrap glasses derived from glass working and in vessel glasses from Al-Raqqa. A beaker, a phial and window glass samples found at Al-Raqqa plot with eastern samples in Figure 6, and in the Samarra correlated group in Figure 5, suggesting that they were imported along the river Euphrates from Samarra to Al-Raqqa some 430 miles away. Two nearly colourless Nishapur beaker fragments (with a yellowish tinge) decorated with applied knobs plot with Al-Raqqa samples and were presumably imported to Nishapur from Al-Raqqa.

Levantine and Egyptian glasses dating to between the late 8th and 15th centuries are united in Figures 5 and 6 by their characteristic low Cr/La and Li/K ratios respectively. Late 8th century glass samples from Khirbat al-Minya are especially well distinguished from most other Levantine glass. Results for the cosmopolitan centres of Beirut and Damascus have the lowest Cs/K ratios and Beirut glasses generally have lower Zr/Ti ratios than found in Damascus glasses. The 14th-15th century mosque lamp glasses attributed to local emirs in Cairo [22] contain amongst the highest Cs/K ratios. The results for two low lead opaque red enamels used to decorate the lamps plot with vessel body glasses suggesting that similar raw materials were used to make the vessel body glasses and the enamels and that they were therefore probably made in the same place.

### **4. Discussion**

Given the large scale of glass production in the Byzantine and Islamic worlds, and the potential for mixing and recycling, our methods and results provide some surprisingly clear compositional

distinctions. They are the first to show clear evidence for broad regional production zones, especially a clear distinction between glasses found in the Levant and in Iran/ Iraq. Had large scale mixing of glasses occurred between glasses made in the Levant, northern Syria and Iran/ Iraq it would have produced far fewer clear elemental groupings for individual site than those in Figures 5 and 6 and there would be more evidence of mixing lines. The correlated group of Samarra samples in Figure 5 could be evidence for mixing with highest and lowest 1000Zr/Ti values representing the end members and those in between the result of mixing different proportions of glasses with end member compositions. The Samarra data also fall into a positively correlated group in Figure 6. If mixing did occur at Samarra it appears to be for glass that was made and used there.

The samples of decorated colourless vessels found at Nishapur, northern Iran provide a useful example of how trace element compositions provide evidence for centres of production and exchange/ trade. Firstly, although colourless cut vessels have predominantly been found in Iraq and Iran, this does not prove that the glass itself was made there or even that glass vessels bearing this decoration were made there. We have shown that relative impurity levels of Cr, Fe, La, Zr and Ti, mainly found in sand, provide a distinction between glasses found in the Levant and Iraq/Iran. Nine Nishapur samples fall into the eastern grouping of Iraqi/ Iranian glasses in Figure 6; four plot in the Levantine area and 2 amongst Al-Raqqa samples. The eastern glasses are united, not only by composition but also by form, because they are all colourless and are decorated by cutting and engraving (5 samples) or are pinch decorated (4 samples; see Fig. 1(c)). The link between these colourless vessels and the eastern zone confirms what has long been suspected, but not proven scientifically before, that the glass used to make the colourless cut and pinch decorated vessels was made in that zone [13-14] and that both its colour and decorations constitute a regional technological specialisation. These vessels dating to the 9th and 10th centuries were preceded and clearly influenced by the production of similar colourless wheel cut plant ash vessels in the same area during the Sasanian period (3rd-7th centuries AD). However, even though similar raw materials would have been used to make them, the Sasanian and our 9th-10th century vessels can mainly be distinguished analytically from ours (see above). This may indicate that the raw materials used derived from slightly different locations.

Four Nishapur glasses fall into the Levantine group in Figures 4, 5 and 6. Significantly these are pale green or pale blue, rather than colourless, and are decorated with threads in pale green, cobalt blue or turquoise colours (See Fig. 1(c)). These results therefore suggest that a Levantine specialisation was the production of thread-decorated vessels.

The massive cosmopolitan settlement of Samarra by the river Tigris was a 9th century capital of the Abbasid caliphate, probably founded in 834-5. Our results provide evidence for another technological variation: they suggest that glass almost certainly made there was used for the manufacture of a relatively wide range of characteristic early Islamic decorative vessel types and wall plaques (see Fig. 1(e)). The colourless, including cut glass, vessels were apparently imported from Nishapur.

Al-Raqqa was also briefly an important city and the caliph resided there in the late 8th and early 9th centuries. The results for Al-Raqqa furnace glasses bolster the case for our interpretation, providing clear provenance information; they fall on quite a tight Cr/Fe correlation line in Figure 4 and Al-Raqqa scrap glasses also plot close to furnace glasses in this Figure. In both Figures 5 and 6 two Al-Raqqa vessel samples, a green bottle rim and colourless bowl rim, plot close to the furnace glasses, showing they were made in Al-Raqqa.

Turning to discussion of the Levantine samples, there is a notable trend in the Cs/K ratios moving from south (Egypt) to north (Beirut and Damascus). The mosque lamps, presumed to have been made in Cairo, have the highest ratio and Beirut and Damascus glasses having the lowest; Khirbat al-Minya glasses fall in between, both geographically and in terms of their Cs/K ratios. Two facet-cut vessels found at Ctesiphon and one from Samarra with low Li/K ratios were made with Levantine glass (Figure 6). The eastern tradition was to make such vessels with colourless glass; significantly these were green. This therefore suggests that raw green furnace glass made in the Levant was exported to Iraq where the vessel was made and decorated in the 'eastern' tradition by cutting. The two Ctesiphon samples plot close to Beirut and Damascus samples in Fig. 6 so the glasses were probably fused in this zone, possibly in one of these important urban centres.

In Figures 5 and 6 results for 14th-15th century Egyptian mosque lamps fall within the clearly defined Levantine production zone yet five are also separated from Khirbat al-Minya, Damascus and Beirut glasses by having high Cs/K values [34].This suggests that the mineral combinations ultimately deposited by the Nile deriving from the East African Highlands (the Blue Nile in Ethiopia and the White Nile in Tanzania, Kenya and Uganda) taken up by plants and deposited in sands are distinct from those used to make glasses from the other 'Levantine' sites [35-36]. Nevertheless it is possible that the glass used to make the mosque lamps was fused outside Egypt (perhaps in the southern Levant). Concentrations of Zr, Ti, Cr and La (Fig. 5) for much earlier (Late Bronze Age) glass mainly associated with probable inland sand sources [37], can be distinguished from most of our Levantine glass data. Evidently the mosque lamp glass was not made in northern Syria, Iraq or Iran. The compositionally well-defined Khirbat al-Minya glasses were probably not made in, for example, Beirut or Damascus, which are further north, but perhaps in an urban centre closer to the site such as Amman or Jerusalem. Trace element analysis of more well dated samples from the Levant should help to substantiate these findings

By using chemical and isotopic analyses (with some exceptions [10]) mainly of raw furnace glasses, it has been suggested that there were two principal production zones for Roman and Byzantine *natron glass* during the first millennium AD, one in Egypt and the other on the Levantine coast [5, 6, 9, 10]. The centralised production model envisages that raw glass was exported from primary production sites to secondary production sites where glasses were remelted and blown into vessels. Chemical sub-types of natron glass can sometimes be associated with coastal furnace sites but in spite of a suggested link between some vessel types/ decorations and chemical compositions [37], so far there is limited compositional evidence [6, 39].

## 5. Conclusions

The trace element analyses of Islamic plant ash glasses from across a broad geographical area in this study provide the first clear evidence for regional production zones in the Levant, northern Syria and in Iraq/ Iran. They also provide evidence for production sub-zones associated with the large cosmopolitan urban hubs with thriving economies supporting the manufacture of a range of materials such as ceramics and glass and supplying local, regional and supra-regional markets. As for natron

glass, a centralised production model within the Levant has recently been suggested for plant ash glass [40]. While it is clear from the data presented here that the Levant was an important production zone, we the production sub-zones associated with urban centres we have detected in the Levant indicate that decentralised production occurred and over a period of c. 800 years. This model of broad production zones and internal sub-zones also applies to areas much further east in Iran and Iraq, as exemplified by separate production associated with Samarra and Ctesiphon, which are only 84 miles apart (see Figure 2). We are also able to discriminate using trace elements between most (earlier) Sasanian plant ash glasses and our later Iraqi and Iranian samples made in the same geographical area. Much of the manufactured glass and vessels appears to have remained in or near the cosmopolitan hubs locations where it was made.

However, in contrast to this, we are able to indicate when glass has travelled between centres linked by the Silk Road across the 2000 mile area. We have shown that glass made in the Levant was exported to Samarra, Ctesiphon and Nishapur, that glass made in Al-Raqqa was exported to Samarra and Nishapur, that glass made in Ctesiphon was exported to Al-Raqqa and that glass made in Nishapur and Samarra was exported to Ctesiphon.

We have detected evidence for technological specialisation. Results from Nishapur and Ctesiphon demonstrate that the centres specialised in producing colourless and pale green wheel cut facetted glass vessels respectively (see Fig. 1(a)). These contrasting results provide evidence for the existence of two separate production centres within the broad eastern zone that specialised in different colours of cut and engraved glass vessels.

The study's supra-regional sampling strategy has highlighted regional differences, including evidence for the specialised production of different glass colours and vessel decorations and has helped to define the Silk Road, linking the 'centre' of the Middle Eastern Islamic world to its 'periphery'. The results have also provided evidence for the existence of technological identities associated with production zones as part of the decentralised production of plant ash glass. Our results can also improve predictions about trade and exchange without scientific analysis. This new evidence for

production zones provides an interesting way forward for the study of ancient glass in relation to production, supply, trade and exchange.

### **Acknowledgements**

We are grateful to Professors Jane Evans and Mark Pearce for reading through this paper and commenting on it. We are also grateful to the University of Nottingham Centre for Advanced Studies for funding this research and to The Museum of Islamic Art in Berlin (especially the Director, Prof. Dr. Stefan Weber), The Museum of Islamic Art in Doha. The Director General of Antiquities for Syria, Dr Sophie Bertier, the Director General of Antiquities in Beirut and Dr. Hans Curvers for giving us permission to take micro-samples of glass for scientific analysis. Simon Chenery published with permission of the Director of the British Geological Survey.

### Figure captions

Figure 1 Photographs of glass from which samples were removed: (a) Facet cut bowl fragments from Ctesiphon in Iraq (samples CTES 15 and 16); (b) Undecorated flask from Khirbat al-Minya in Israel (sample KAM 11); (c) Pinch decorated beaker rim and trail decorated bowl rim fragment from Nishapur, Iran (Samples NISH 9 and 17); (d) Pinched decorated bowl rim and scratch decorated fragment from Samarra, Iraq (Samples SAM 11 and 15); (e) A cameo decorated bowl rim fragment and a wall plate from Samarra, Iraq (samples SAM 17 and 35); (f) One of hundreds of glass furnace floor fragments from Al-Raqqa, Syria. This one has raw purple glass attached to it (sample RAQ 38). Photographs: J. Henderson.

Fig 2 Location map showing where the glass samples were derived from (the locations of Baghdad and Tehran are also given)

Fig 3 Weight % MgO versus CaO for glasses in this study compared with analyses of glasses from Nishapur, Iran [16], Raya, Egypt [19], the Serç Limani shipwreck [25], enamelled vessel glasses [29- 30] and raw glass from Banias [5]. The parallel lines enclose glass mainly from northern Syria and enamelled glasses. Glasses mainly from Iran and Iraq plot below the line and those from the Levant above it.

Fig 4 Fe versus Cr concentrations (mg/kg) in the samples analysed

Figure 5 Cr/La versus 1000Zr/Ti ratios in the samples analysed

Fig 6 Li/K versus Cs/K ratios in the samples analysed

List of appendices

Appendix A Comparison between our LA-ICP-MS analyses of the Corning B standard, the expected composition [24] and Wagner et al.'s analytical assessment [27].

Appendix B Electron probe microanalyses (wt % oxide) of the samples analysed. Sam= Samarra; Kam= Khirbat al-Minya; Nish= Nishapur; Ctes= Ctesiphon; Bei= Beirut; Dam= Damascus. 0= below level of detection

Appendices C.1-C.8 LA-ICP-MS analyses of glass samples

### **References**

(1) S. Carboni, D. Whitehouse, Glass of the sultans, Metropolitan Museum of Art, New York, 2001

(2) AnJiayao, Dated Islamic glass in China, Bulletin of the Asia Institutes 5 (1991) 123-138.

(3) E.V. Sayre and R.W. Smith**,** Compositional categories of ancient glass, *Science* 133 (1961) 1824– 6.

(4) J. Henderson, Ancient Glass, an interdisciplinary exploration, Cambridge University Press, New York and Cambridge, 2013

(5) I.C. Freestone, Y. Gorin-Rosen, M.J. Hughes, Primary glass from Israel and the production of glass in late antiquity and the early Islamic period, in: Nenna M.-D. (Ed.), La Route du verre: Ateliers primaires et secondaires du second millénaire av. J.-C. au Moyen Age, Maison de l'Orient Méditerraneéan-Jean Pouilloux, Lyon, 2000, pp. 65–84.

(6) C.M. Jackson, Making colourless glass in the Roman world, Archaeometry 47 (2005) 763–80.

(7) R. Arletti, C. Giacobbe, S. Quartieri, G. Sabatino, G. Tigano, M. Triscari, G. Vezzalini, Archaeometrical investigation of Sicilian early Byzantine glass: chemical and spectroscopic data, Archaeometry 52, 1 (2010) 99–114.

(8) N. Schibille, Late Byzantine Mineral Soda High Alumina Glasses from Asia Minor: A New Primary Glass Production Group, Plos One (2011).

(9) I.C. Freestone, K.A. Leslie, M. Thirlwell, Y. Gorin-Rosen, Strontium isotopes in the investigation of early glass production: Byzantine and early Islamic glass from the Near East, Archaeometry 45 (2003) 19–32.

**(**10) P. Degryse P ed., [Glass Making in the Greco-Roman World: Results of the ARCHGLASS project,](http://books.google.co.uk/books?hl=en&lr=&id=I194BgAAQBAJ&oi=fnd&pg=PA11&dq=degryse+roman+hellenistic+leuven+university+press+2014&ots=XGWqiW9aUC&sig=mk3oM_o1g6nrsW6-aLE-XQkU4-Q) Leuven University Press, Leuven, 2015.

(11) V. [Devulder,](http://pubs.acs.org/action/doSearch?ContribStored=Devulder%2C+V) P. [Degryse,](http://pubs.acs.org/action/doSearch?ContribStored=Degryse%2C+P) F. [Vanhaecke](http://pubs.acs.org/action/doSearch?ContribStored=Vanhaecke%2C+F) F, Development of a Novel Method for Unravelling the Origin of Natron Flux Used in Roman Glass Production Based on B Isotopic Analysis via Multicollector Inductively Coupled Plasma Mass Spectrometry, Anal. Chem. 85 (2013) 12077–12084.

(12) R. Irwin R, A note on textual sources for the history of glass, in: R. Ward (Ed.), Gilded and enameled glass from the Middle East*,* The British Museum, London, 1998, pp. 24–26.

(13) S. Carboni, Glass from Islamic lands, the al-Sabah collection, Thames and Hudson, London, 2001.

(14) J. Kröger J, Nishapur: Glass of the early Islamic period*,* Metropolitan Museum of Art, New York, 1995.

(15) G.T. Scanlon, R. Pinder-Wilson, Fustat glass of the early Islamic period. Finds excavated by the American Research Center in Egypt 1964–1980, Altajir World of Islam Trust, London, 2001.

(16) R.H. Brill R H, Chemical analyses of some glass fragments from Nishapur in the Corning Museum of Glass in: J Kröger, Nishapur: Glass of the Early Islamic Period, Appendix 3, The Metropolitan Museum of Art, New York, 1995, pp. 211–33.

(17) R.H. Brill, Some Thoughts on the Chemistry and Technology of Islamic Glass, in: S. Carboni, D. Whitehouse, Glass of the Sultans, The Metropolitan Museum of Art in association with The Corning Museum of Glass, Benaki Museum, and Yale University Press, New York, 2001, pp. 25–45.

(18) J. Henderson, S. McLoughlin, D. McPhail, Radical changes in Islamic glass technology: evidence for conservatism and experimentation with new glass recipes from early and middle Islamic Raqqa, Syria, Archaeometry 46 (2004) 439–68.

(19) N. Kato, I. Nakai,Y. Shindo, Transitions in Islamic plant ash glass vessels: On-site chemical analyses conducted at the Raya/al Tur area on the Sinai Peninsula, Egypt. J. Archaeol. Sci. 37 (2010) 1381–95.

(20) J. Henderson, J. Evans, Y. Barkoudah, The roots of provenance: glass, plants and isotopes in the Islamic Middle East, Antiquity 83 (2009) 414–29.

(21) J. Henderson J, Archaeological and scientific evidence for the production of early Islamic glass in al-Raq*qa,* Syria*,* Levant 31 (1999) 225–40.

(22) A. Meek, J. Henderson, J. Evans, Isotope analysis of English forest glass from the Weald and Staffordshire, J. Anal. Atomic Spec., 27 (2012) 786–795.

(23) R.H. Brill, Chemical analyses of early glasses, volume 2, Tables of analyses, The Corning Museum of glass, Corning, New York 1999.

(24) B. Wagner, A. Nowak, E. Bulska, K. Hametner, D. Günther, Critical assessment of the elemental composition of Corning archaeological reference glasses by LA-ICP-MS, Anal. Bioanal. Chem. 402 (2012),1667–1677.

(25) J. Henderson, Glass trade and chemical analysis: A possible model for Islamic glass production, in D. Foy, M.-D. Nenna (Eds.), Échanges et commerce du verre dans le monde antique*,* Actes du colloque de l'Association Francaise pour l'Archéologie du Verre, Aix-en-Provence et Marseille, 7–9 June 2001, Éditions Monique Mergoil, Montagnac, 2003, pp. 109–23.

(26) J. Henderson, J.A. Allan, Enamels on Ayyubid and Mamluk glass fragments, Archaeomaterials 4 (1990) 167–83.

(27) J. Henderson, Investigations into marvered glass II, in J. Allan (Ed.) Islamic Art in the Ashmolean Museum, Oxford Studies in Islamic Art, vol. 10, part 1, Oxford, Oxford University Press, 1995, pp. 31– 50.

(28) P. Mirti, M. Pace, M. M. Negro Ponzi, M. Aceto, ICP-MS analysis of glass fragments of Parthian and Sasanian epoch from Seleucia and VehArdašīr (central Iraq)*,* Archaeometry *50 (2008) 429–50.*

(32) R.H. Brill, Chemical analyses of some Sasanian glasses from Iraq, in D. Whitehouse, Sasanian and Post-Sasanian glass in the Corning Museum of Glass, The Corning Museum of Glass, Corning, New York, 2005, pp. 85-88.

(33) Y. Barkoudah, J. Henderson, The use of halophytic plants in the manufacture of ancient glass: ethnographic evidence and the scientific analysis of plant ashes, J. Glass Studies 48 (2006) 297-321.

(34) J. Henderson, S. Chenery, J. Kröger, E. Faber, Glass provenance and the Levantine Silk Road: the use of trace element analysis, in: Gan Fuxi, Li Quinghui*,* Julian Henderson (Eds.) Recent progress in scientific research of ancient glasses and glazes, World Scientific Publishing Co., Singapore, in press.

(35) Y. Be'eri-Shlevin, D. Avigad, A. Gerdes, O. Zlatkin, Detrital zircon U-Pb-Hf systematics of Israeli coastal sands: new perspectives on the provenance of Nile sediments, J. Geol. Soc., 171 (1) (2014) 107–116.

(36) M. Krom, R. Cliff, L. Eijsink, B. Herut, R. Chester, The characterisation of Saharan dusts and Nile particulate matter in surface sediments from the Levantine basin using Sr isotopes, Marine Geol., 155 (3-4) (1999) 319–330.

(37) A.J. Shortland**,** N. Rogers**,** K. Eremin**,** Trace element discriminants between Egyptian and Mesopotamian Late Bronze Age glasses, J. Archaeol. Sci*.* 34 (2007) 781–9.

(38) C. Jackson and H. Foster, Provenance studies and Roman glass, in J. Bayley, I. Freestone and C. Jackson (Eds.), Glass of the Roman World, Oxbow Books, Oxford and Philadelphia, 2015, 44-56.

(39) M.J. Baxter, H.E.M. Cool, C.M. Jackson, Further studies in the compositional variability of colourless Romano-British vessel glass, Archaeometry 47 (2005) 47-68.

(40) M. Phelps, I. Freestone, Y. Gorin-Rosen, B. Gratuze, J. Langton, Technological change and provenance of glass in Early Islamic Palestine, 20th Congress of the International Association for the History of Glass, Friborg-Romont, Switzerland, Programme and Abstracts, 2015, p. 157.

Appendix A: Table of LA-ICP-MS results for Corning 'B' glass

**Assumed Si Concentration: 287706 mg/kg**







كان المناسب المعامل التي التي التي التي المعامل المعامل المعامل المعامل المعامل المعامل المعامل المعامل المعامل

















