Down in the dumps: Analysis of glass production debris from Petrie's excavations at Amarna

Vanessa Muros[1], Nicole Little[2], Yuan Lin[3] and Patrick Boehnke[4]

[1]Conservation Specialist/Lecturer, UCLA/Getty Conservation Program

[2]Physical Scientist, Smithsonian's Museum Conservation Institute

[3]PhD Candidate, Dept. of Materials Science and Engineering, UCLA

[4]T.C. Chamberlain Postdoctoral Fellow, Dept. of the Geophysical Sciences, University of Chicago

Abstract

Sir Flinders Petrie's excavations at Tell el-Amarna in Egypt (1891-1892) uncovered a large number of glass finds and vitreous debris from areas identified as palace trash heaps and industrial buildings, suggesting that glass was produced at the site as early as the fourteenth century BC. His findings, combined with those from recent archaeological investigations and chemical analyses, highlight the important role Amarna played in early glass technology and its significance as a location for glass production, both locally and abroad, during thelatter part of the Late Bronze Age (sixteenth-eleventh century BC).

Though Petrie found evidence of different stages of glass production at the site, it is not clear whether these finds indicate glassmaking or working. Recent excavations at Amarna have shed some light on the types of activities that took place there. However, due to a lack of thorough recording by Petrie of the areas he excavated, and the fact that many of these early glasses have not been fully analyzed, questions still remain about glass production at the site and how these materials should be interpreted within the larger context of the Egyptian glass industry.

The research conducted aims to provide further insight into the production of vitreous materials at Amarna through the instrumental analysis of glass debris excavated by Petrie housed in the Penn Museum. Using a multi-analytical approach (pXRF, SEM-EDS, EPMA), the glass was characterized to identify the raw materials utilized and determine whether the debris belongs to primary glass made at Amarna or was imported to the site to be worked into finished objects. The results of this study will be used as comparanda to aid in the interpretation of glass found at other LBA sites adding to the broader understanding of glassmaking during this time period and the long-distance trade networks used to move this material across the eastern Mediterranean.

Introduction

Glass was first made in the Near East around the third to early second millennium BC (Moorey 1999). After this period, the occurrence of glass in the archaeological record is sporadic until the sixteenth century BC when a range of jewelry, items of personal adornment and vessels were made in production centers located in the Near East and Egypt (Moorey 1999; Shortland 2012). These centers created both finished glass objects and glass ingots, which were sent across the

eastern Mediterranean via an extensive trade network (Jackson and Nicholson 2010; Shortland 2012).

Though glass objects have been found dating to the Late Bronze Age (sixteenth-eleventh century BC) in Northern Iraq, Syria, Greece and Egypt, evidence for the exact location where glass was produced is scarce. Using textual sources or excavated material, possible glassmaking centers have been identified at sites such as Tell Brak, Nuzi, Malkata, Amarna and Qantir (Moorey 1999; Shortland 2012) (fig. 1). However, due tothe lack of archaeological context for many early glass finds or clear evidence of the physical remains of activities associated with glassmaking, questions remain regarding glass production during this period. Continued excavation and research at these sites, along with re-examination of previously excavated material, is needed to help further clarify the LBA glass industry.

<Figure 1 here>

One of the early glass production sites which has been the focus of continued study is the site of Tell el-Amarna, Egypt. Excavated by Sir Flinders Petrie in 1891, Amarna was identified as a site that played a major role in the Egyptian glass industry during the LBA. Petrie uncovered evidence for both faience and glass production and determined that the site was involved in both glassmaking and glassworking. Excavations at Amarna have continued since the first systematic investigations took place there in the nineteenth century, and the finds Petrie recovered have been the subject of further study and analysis (Nichsolon 2007; Smirniou and Rehren 2011; Hodgkinson, personal communication 2016). Despite this recent work, there is still some

uncertainty about the nature of glass production at Amarna and Petrie's interpretations of what he found there.

The research described in this paper tries to address some of these outstanding questions and provide additional information on LBA glass production in Egypt. More specifically, the work presented aims to identify the raw materials and technology used to manufacture a group of glass finds from Petrie's excavations at Amarna, currently housed at the Penn Museum. The objects selected represent debris collected from waste heaps associated with glass workshops. Through the application of multiple analytical techniques the composition of the glass was identified in order todetermine whether this material was made at Amarna or was imported to be worked into finished objects at the site.

<u>The Nature of Glass and Glass Production</u>

Glass iscomprised of silica (SiO_2) which comes either from sand or quartz pebbles. In the LBA, quartz pebbles were primarily used (Smirniou and Rehren 2011). Additional raw materials, in the form of alkali earths, must be added to change the properties of the silica network in order to make glass. The most commonly used network modifiers during the LBA contained the elements sodium (Na), potassium (K), magnesium (Mg) and calcium (Ca) (Shortland 2012). The addition of soda (Na_2O) or potash (K_2O) act as a flux and lower the melting point of the silica. Silica melts at around 1700°C, a high temperature that would have been difficult to obtain with LBA furnaces (Smirniou and Rehren 2011). By adding a flux, the melting temperature of silica drops to around 1000-1100°C, or possibly even lower (800-900°C), depending on the composition of the glass and type of flux used (Rehren 2000; Turner 1954, 1956). The addition of magnesia

(MgO) and lime (CaO), which come in with the flux and silica source, make the glass more stable and less water-soluble.

The flux used in LBA glass is plant ash derived from burning halophytic plants that grow in areas of high salinity (Henderson 2012). These plants provide the source of the potash, and are also high in soda. The average composition for this glass is 15-20% Na_2O, 2-8% K_2O, 4-8% CaO and 2-8% MgO (Henderson 2012; Nicholson 2007; Shortland 2012). Plant ash is used up until around 1000BC, when it is replaced by the mineral evaporite natron ($Na_2CO_3 \cdot 10H_2O$) (Henderson 2012). The switch to natron creates a glass with lower concentrations of potash, magnesia and lime. The composition of natron glass averages 15-20% Na_2O, 0.1-1.5% K_2O, 1-5% CaO and 0.5-2.5% MgO (Henderson 2012).

The last components added to glass are metal oxides that act as a colorant or opacifier. Because of impurities in the raw material, namely iron, glass made without the addition of a colorant willoften have a green or blue-green tint to it. Therefore other metal oxides need to be added to impart a different color, opacity or to act as a decolorizer (Shortland 2012).

In*glassmaking* (primary production) raw materials are heated and melted to produce raw glass. Petrie (1894) had suggested that glass was made in two-steps and current thought supports that idea (Rehren 2000; Smirniou and Rehren 2011).The raw materials are first placed in a crucible, lined with lime based-parting layer, and heated at a low temperature to create a semi-fused glass in a process called fritting (Smirniou and Rehren 2011). This semi-fused glass, or frit, is removed from the crucible, crushed and then refired at a higher temperature to form fully fused glass. The

stage at which the colorant was added is unclear.Colorants could have been added initially with the raw materials, when melting the semi-fused glass or even in a third step where the colorants were added to fully fused colorless glass (Petrie 1894; Smirniou and Rehren 2011).

*Glassworking (*or secondary production) refers to the stage whenraw glass, as a lump or ingot, is worked to make a finished object. Thoughglassmaking and working can take place at the same site, studies of later glass production centers show that these activitiesgenerally occurred at different locations (Shortland 2012), so that sites that worked glass did not necessarily make the material. The current evidence for the LBA glass industry suggests only a few sites were making glass, possibly each site specializing in a few specific colors (Smirniou and Rehren 2011). Glass was worked at other sites that did not necessarily have to be located near primary production centers. The discovery of 175 glass ingots from the Uluburun shipwreck (1300 BC), which were made in Egypt and Mesopotamia, shows there was long distance trade of glass ingots sent across the eastern Mediterranean to be worked into finished objects (Jackson and Nicholson 2010).

Because different sites focused on specific aspects of glass production it is important to understand the distinction between primary and secondary production in order to accurately interpret the archaeological remains of this industry. Evidence of glass workshops in the archaeological record is rare, and much more so for glassmaking sites. Some archaeological evidence for glassmaking in Egypt has been found at sites like Malkata, Amarna and Qantir (Smirniou and Rehren 2011). In the Near East however, no primary production workshops have been found and evidence for this activity is drawn from the early finds of glass located in the region and textual evidence (Moorey 1999; Nichoslon 2007).

Not only does the scant archeological evidence for these activities make identification difficult, but also similarities between the physical remains from both types of workshopscomplicate interpretation (Nicholson 2007; Shortland 2012). Both glassmaking and working areas contain furnaces that would differ based on the temperatures needed for each stage, but could physically look similar. Crucibles and metal tools would be found at both types of workshops. Glass debris could be found at bothsites such as glass ingots, rods or strips. Glassworking sites, however, would also contain misshapen objects or artifacts showing flaws or mistakes in manufacture.To truly differentiate the two types of production the raw materials used in glassmaking would have to be found; finding crucibles with failed batches of glass or semi-fused glass would be indicative of primary production. Unfortunately these materials do not preserve well in the archaeological record and very little direct evidence for primary production has been uncovered.

Petrie's Excavations at Amarna

Tell el-Amarna, or Akhetaten, was the capital of Egypt during the reign of Amenhotep the IV who became ruler of Egypt in about 1347 BC. Amenhotep IV, later known as Akhenaten, broke from the previous religious traditions upheld by his predecessors and began worshipping the god Aten (Kemp 2014). He built a new capital for the worship of this god because he wanted a site that was "untainted by the worship of previous gods" (Shortland 2012: 69).

Amarna remained the capital of Egypt for about 15 years until the death of Akhenaten when the capital was moved back to Thebes. During Akhenaten's brief reign, Amarna flourished. Temples, palaces, administrative buildings, industrial areas and living quarters were built. Though Amarna is not the earliest site in Egypt where glass was found, that is the site of Malkata

(1391-1353 BC), the number of glass finds and the scale of production of vitreous materials at the site was unprecedented (Shortland 2012).

Petrie excavated Amarna from 1891-1892 (Petrie 1894). Work at the site had beenpreviously undertaken, but Petrie's work represented the first systematic excavation of the site. Petrie's area of focus was the "Central City" where he investigated the "Great Palace" and the surrounding areas (Kemp 2014) (fig. 2). It is at the palace where he first discovered glass, in the form of broken vessels. In the area outside the palace walls, in a clearing about "3 furlongs" (or 1980 feet) away, he foundthe "rubbish heaps where waste was thrown from the palace" (Petrie 1894: 15) (fig. 3). In these trash heaps (or "palace dumps"),which were about 600 x 400 ft and anywhere from 4 ft deep to just a "sprinkling" of material on the surface, he discovered a large amount of glass fragments: approximately 750, which he estimated corresponds to about 150 vessels(Petrie 1894: 16). Because of their proximity to the palace, he concluded that glass was a high status material linked to the palaces and the elite.

<Figure 2 here>

<Figure 3 here>

Petrie discovered more evidence of glass, and faience, production, in what he identified as an industrial area (Petrie 1894). He described finding the remains of three or four glass factories and two large glazing works, the latter of which were likely used to make faience objects. There were no workrooms preserved but waste heaps and debris indicated the manufacture of vitreous materials. Some of these remains included "fritting pans", or fragments of ceramic vessels which contained semi-fused glass, silica grains or frothy-looking glass**.** He found cylindrical jars with

drips of glass on the sides he said held up the fritting pans during firing. There were quartz

pebbles with vitreous material on the surface, thought to line the floor of the furnaces. He

thought these pebbles also served as the silica source for the glass.Misshapen beads, somewith

the wire used to make them still inside, glass drips, strips and fragments of finished objects were

also uncovered.

Based on his findings, Petrie concluded that glass was being both made and worked at Amarna.

His interpretations however, were not completely accepted at first. Excavations have continued

at the site with a focus on understanding glass production and the finds from Petrie's excavation

have been re-examined (Nicholson 2007; Smirniou and Rehren 2011). Additional evidence for

glass production and working debris was also found (Hodgkinson 2015; Shortland 2012).

Excavations undertaken in 1993-2003, in the area thought to be the location of Petrie's glass

factories, uncovered two furnaces that could have been capable of producing glass (Nicholson

2007). A fragment of a crucible with semi-finished glass inside was discovered during these

excavations. Analysis of some of Petrie's "frothy" looking glass and white working waste

showed these were semi-finished glasses indicative of an early stage of glassmaking (Smirniou

and Rehren 2011). Despite these recent findings, there is still some uncertainty about the

interpretations Petrie provided for the material he discovered (Shortland 2012; Smirniou and

Rehren 2010).

Many of the questions surrounding glass production at Amarna arise from the difficulty in

correlating the information Petrie published with the archaeological evidence at the site

(Nicholson 2007). Though Petrie worked extensively and published information on his

excavations quickly, the notes he took do not serve as a very accurate record of what he found. For example the exact location of the "factories" he discovered is unknown. The area that Petrie describes as the industrial sector is not recorded on the site plan he created. There is a section on the site plan labeled "MOULDS" which is where he discovered many molds for amulet making (Petrie 1894: PL.XXXV)(fig. 3).Based on where this area is on the site plan, and the types of finds, it is possible that this could be where he found the debris from the factories (Nicholson 2007).More recent work at the site however suggests other possible locations for Petrie's workshops (Hodgkinson 2015).

In addition to leaving some information out of the site plan, Petrie did not record the provenience of specific finds (Nicholson 2007). He collected a large amount of material from the site and transported it out of Egypt as a large group, with no contextual information. These finds were then split among the museums that sponsored Petrie's excavations, and the number of museums that hold this material is quite extensive. Though excavations continued at Amarna after Petrie, at the moment, the majority of the glass finds available for study outside of Egypt are those from the Petrie excavations (Shortland 2012).

Analysis of Glass Debris from Amarna

Glass samples

The glass debris analyzed for this study is part of a larger group of material that the Penn Museum purchased from Petriein 1893 (Online Collection 2016). The museum had an existing relationship with Petrie prior to the acquisition of the Amarna finds in that they provided financial support for his Amarna excavations(Egyptian Section 2016).

The objects analyzed consist of glass rods and strips from waste heaps and are likely to have been discarded during the working of glass (fig. 4). Twenty-six pieces of glass were selected for non-invasive, qualitative analysis. From this group, 11 rods were sampled for quantitative analysis. Several colors were chosen in order to incorporate as broad a range of raw materials as possible.

<Figure 4 here>

Characterization Methods

Several analytical techniques were used to characterize the glassworking debris. A summary of the techniques applied to each object/sample can be found in table 1.

Optical Microscopy

A stereomicroscope was used to examine the glass rods prior to sampling and before mounting. After mounting and polishing, the samples were examined and photographed using A Keyence VHX-1000 digital microscope (50-200x magnification)at the Molecular and Nano Archaeology Lab, UCLA.

pXRF

A Bruker Tracer III-SD portable x-ray fluorescence (pXRF) spectrometer (silicon drift detector, rhodium (Rh) target x-ray tube with palladium slits), belonging to the Penn Museum's Conservation Laboratory was used to obtain qualitative data on the 26 glass strips and rods. A 10mm diameter area on the surface of each object, which was free of soil or weathering, was

chosen for analysis. Data was acquired at 40kV/11µA, with a 1mm titanium (Ti) /12mm

aluminum (Al) filter for high Z elements andat 15kV/25µA, with 1mm Ti filter for light element,

with a detectiontime of 180 seconds. The spectra collected were processed with the program

S1PXRF (version 3.8.3) from Bruker AXS. Semi-quantitative analysis was conducted by

calculating the net photon count for each element using Bayesian deconvolution and normalizing

the data to the Rh peak using Artax (v. 7.1.0.2) from Bruker.

Sampling and mounting

Eleven glass rods were sampled for compositional analysis using a variable speed hand drill

equipped with a diamond core drill bit (2mm diameter). The samples were taken from the end of

the glass rod and each 2mm piece taken included a portion of the cross-section of the rod. The

samples were placed in a 1-inch Teflon (PTFE) ring and embedded in Struers EpoFix Resin. The

mounted samples were ground using aluminum oxide paper (400-1200 grit) and polished using

Buehler's Metadi diamond suspensions (6 and 1 micron) on Buehler Mastertex cloths.

EPMA-WDS

Electron probe microanalysis (EPMA) with wave dispersive spectroscopy (WDS) was

undertaken to quantify major and minor elements using a JEOL JXA-8200 Superprobe electron

microprobe analyzer at the Dept. of Earth, Space and Planetary Sciences, UCLA. WDS analysis

was performed at an accelerating voltage of 15 kV and a current of 15 nA. Five areas on each

sample, with a spot size of about 10 µm, were analyzed and an average weight percent (wt%)

concentration for each oxide of interest calculated using geological standards commonly used by

UCLA's Dept. of Earth, Space and Planetary Sciences. External glass standards (Corning A, B,

C, and NIST 612) were used to check the accuracy of the results (table2).ZAF correction was applied to all WDS analyses.

<u>VP-SEM-EDS</u>

Avariable pressure scanning electron microscope (VP-SEM) equipped with an energy dispersive x-ray spectrometer (EDS) was used to analyzedifferences between the composition of the bulk glass and any inclusions, opacifiers, or unmelted/unreacted materials from the batch glass. A Nova Nano SEM 230 SEM at the Molecular and Nano Archaeology Laboratory, UCLA was used for imaging in secondary electron (SE) mode using a low vacuum detector (LVD). Elemental analysis was performed with a Thermo Scientific NORAN™ System 7, X-ray EDS. The spectra were processed using the NSS Spectral Imaging System software from Thermo Scientific, Inc. Three areas on each sample, measuring approximately 200 μm^2, were analyzed withan accelerating voltage of 20kV, beam current of 10 nA and working distance of 5mm. Spot analysis was also performed. The concentrations obtained for the weight percent (wt%) of each oxide were averaged and normalized to 100% External glass standards (Corning A, B, C and NIST 612) were used to check the accuracy of the EDS analysis(table 3). ZAF correction was applied to all EDS analyses.

Results and Discussion

<u>Optical Microscopy</u>

Examination of the cross-sections of the 11 mounted samples revealed interesting information about the coloration and manufacture of the rods. The colorant did not seem to be uniform across the sample and appeared streaky or mottled. In some cases the color looks to have

beenincorporated into a colorless or lightly colored base glass, possibly supporting the suggestion that LBA glass was initially colorless with the colorant added at a later stage (Smirniou and Rehren 2011). Elongated air bubbles were visible indicating the rods were pulled during manufacture.

Mounting and polishing the samples allowed for differences in colors that appeared similar macroscopically to be observed. The two yellow opaque glasses, E843H and E1008C1, were made using the addition of a yellow opacifier, lead antimonate (see pXRF results). In the sample from E843H, the yellow opacifier is mixed into what appears to be colorless glass (fig. 5). The size of the opacifier crystals vary across the sample (a few microns to 75 microns). Some appear bright yellow and others a mixture of golden yellow to a more brown tone. The other yellow opaque glass rod examined, E1008C1, has smaller lead antimonate inclusions (<45 μm) and the yellow color is somewhat more evenly distributed. Despite these differences in the size and distribution of the opacifier, the overallcoloring effect is the same.

<Figure 5 here>

The sections also show that different colored glasses were mixed together to create a particular color. Opaque green glass made by mixing blue and opaque yellow glass (Shortland 2012). Rod E843A, an opaque green color, consists of a green-base glass with yellow lead antimonate added. If the base glass was made through a mixture of blue and yellow glass, the blue glass is no longer visible. Rod E1008D is made using a light blue base glass with a yellow opacifier, in addition to fragments of a red opaque glass containing white inclusions (fig. 6). The Penn Museum catalog describes the color as "green" but the glass appears more turquoise in color. It is not clear what

tonal effect the addition of yellow and red to the glass was supposed to achieve but the mixture of different materials is interesting and should be investigated further.

<Figure 6 here>

pXRF

The pXRF results obtained provide initial qualitative data on the possible colorants and opacifiers used to make the rods and strips (table 4). All the elements detected are typical for colorants and opacifiers used during the LBA. Some of the results are discussed below.

Blue

All dark blue glasses (E843D, E844G-M) were colored using a mixture of copper (Cu) and cobalt (Co). The other blue glasses (opaque and translucent) contain only copper as the colorant. This includes rod E1008G which is described in the online catalog as "transparent", interpreted as meaning colorless (Online Collection 2016). The rod actually appears very light blue in color and showed an intense Cu peak**.**

All the blue glasses also contained tin (Sn) and lead (Pb). The identification of these elements, and their association with Cu, suggests the use of bronze scrap or corrosion as the source of the copper colorant (Nicholson 2007). The presence of Sn in Cu-colored glass has only been found in glass made in Egypt (Shortland and Eremin 2006). Mesopotamian Cu glass does not contain Sn suggesting a pure source, such as a mineral, for the copper colorant. Other rods and strips that had Cu as a major contributor to the color also contained Sn and Pb (table 4).

Six of the blue glasses analyzed contained antimony(Sb) even though the glasses do not appear opaque. All the Co-Cu glasses contained this element as does E1008G, the "transparent" rod. Antimony was used as a decolorizer, though was more commonly used this way in later periods (sixth-fifth century BC) (Henderson 2012). It is possible that it could have been added to E1008G in an attempt to make colorless glass. The reason for the addition of Sb to the dark blue glasses is unclear.

Brown, yellow and gray

A few of the glass pieces analyzed seem to be colored primarily with iron (Fe) despite the different colors produced. These colors include dark brown (E843E, E843K), golden yellow (E1008A), and gray (E843M). Iron has been known to produce various colors of glass based on the oxidation state of Fe present, either ferric or ferrous, and the ratio of the two, as well as the firing conditions, length of firing, and the interaction of iron with other elements present in the glass (Henderson 2012; Nicholson 2007; Shortland 2012)

Black

The black glass (844E, 1008E) consists of a mix of mineral colorants. Manganese (Mn) is one of the major elements present in these objects and was used to make black and purple glasses (Nicholson 2007). An intense Cu peak was also detected which would have provided a blue color to the glass. Sn and Pb were also found in these two pieces. A mixture of Mn and Cu colorants may have been used to create a darker more intense tone to the glass.

Opaque colors

All opaque glass analyzed contained Sb. The white opaque glasses (E1008C.2, E1008I.1) is

likely opacified with calcium antimonate based on the intensity of both the Ca and Sb peak and

descriptions of white opaque glasses in the literature (Nicholson 2007). The blue opaque glass

strip (E844A) would have also been opacified with calcium antimonate. Yellow

(E843H,E1008C.1) and green opaque (E843A,E844L, E844O, E1008F) glasses were colored

using lead antimonate because of the prominent peaks for both Pb and Sb (Nicholson 2007). For

the green opaque glasses, a Cu colorant was used to produce the blue hue needed to make green.

The green rod E843A also contained Sn and Pb. E1008F contained Pb from the yellow opacifier,

but had no Sn.

The red opaque glasses (E844D, E1008B) did have a small peak for Sb, however unlike the other

opaque glasses, antimony would not have created the opacity observed.Analysis of red opaque

glasses from Egyptian and Mesopotamian sites has found that the opacity is produced by small

particles of either copper or cuprite in the glass (Freestone 1987; Rehren 2000). Antimony was

also found in these glasses but the role it played in the glass is not clear. One suggestion is that it

helped in the reduction of copper oxides in order to produce the color (Freestone 1987). Lead has

also been found in these glasses, it may also have been added to aid in the production of particles

or crystals to increase the opacity.

Semi-quantitative analysis of blue glasses

Quantitative analysis could not be performed on the strips and rods using pXRF, and not all the

rods could be sampled, thereforesemi-quantitative analysis was undertaken using net photon

counts calculated from the pXRF data collected (table 5). There are several factors that can affect

the pXRF results, such as heterogeneity of the material, surface geometry and deterioration/alteration of the surface (Shugar 2013). However the technique is non-destructive making it advantageous to use on museum collections. PXRF analysis, employing a methodological approach that minimizes many of the factors that can influence the results, would allow for a general intrasite comparison of the glass rods. Looking at the elemental photon counts could identify differences between colors that looked similar that suggests different compositions or sources of raw materials. The results could then be used to guide future sampling and analysis.

The focus of the semi-quantitative analysis was the Co-Cu rods and strips. Analytical studies have found that cobalt-colored glass has a distinct composition which is in part due to the cobalt source that contributes a series of associated elements such as Ni, Zn, Fe, Al and Mn (Nicholson 2007; Rehren 2000; Kaczymarczyk 1986). Glasses that contain cobalt obtained from alum sources in the Western Desert of Egypt have elevated levels of alumina and magnesia (Kaczymarczyk 1986; Nicholson 2007; Rehren 2000; Smirniou and Rehren 2013).The presence of these elements, and their concentrations, has been used to determine if the cobalt source comes from Mesopotamia or Egypt.

Co-blue glasses also have lower concentrations of potash in the bulk composition (Nicholson 2007; Rehren 2001; Shortland and Tite 2000). Though LBA glasses contain a range of potash levels, Co-blue glasses have K_2O values below 2%. The reason is for this is unknown but could be due to the use of a different alkali or to the way the alum was processed (Shortland and Tite 2000). Other colors have variable potash levels similar to those seen in the Co-blue glasses.

Therefore although dark blue glasses colored with cobalt seem to be low in potash, not all low potash glasses are necessarily Co-blue (Nicholson 2007).

The pXRF data collected on the Penn Museum dark blue glasses was examined to look for these compositional characteristics of Co glasses described in the literature. The net photon counts of Mg and K, elements introduced through the flux used, were compared. In the bivariate plot of Mg versus K counts, the Co-Cu colored glasses (E843D, E844G,H, J and M) have a ratio of Mg/K distinct from the lighter blue Cu glasses (E1008D, G, H) (fig. 7). However the K values of the 5 dark glasses fall within the ranges observed for other colors of glass. Therefore though the Co-Cu blue glasses seem to be different from the translucent and opaque Cu blue glasses, the ratio of Mg/K is not very distinct from the other colors analyzed.

\<Figure 7 here\>

Since glasses made using the Egyptian cobalt sourcetend to be higher in Al and Mg, a bivariate plot of the counts of these elements was created to determine if this pattern was observed with the Amarna Co-Cu glasses.Four dark blue glasses (E844G,H, J and M) had the highest Al values **\<Figure 8 here\>.**However, a fifth dark blue rod, E843D, has lower counts of both Al and Mg similar to some of the other colors, such as the opaque green glasses (E843A and L). This could indicate a different source for the colorants across the dark blue glasses. Further analysis should be conducted on the dark blue glasses to more accurately identify compositional differences between them.

EPMA-WDS

The bulk composition of the 11 rods analyzed fit the typical composition of LBA plant ash glass(table 6). The soda content averaged 18-21% and the potash 1.2-4%. These concentrations are similar to published Egyptian, Mesopotamian, and Mycenaean glass data from this time period, as well as from glass ingots recovered from the Uluburun shipwreck (Jackson and Nicholson 2010; Nicholson 2007; Nikita and Henderson 2006; Shortland and Eremin 2006; Smirniou et al. 2012) (fig. 9). The magnesia levels (3.3-5.7%) as well as the CaO values (5.2-8.8%) were within the range of published values for glass from Amarna and other LBA sites. A yellow opaque rod, E1000C1, was the only sample that exhibited a low value for soda, averaging 15.47%. However, it is still within the range of soda values detected in glasses from this time period (Nicholson 2007).

<Figure 9 here>.

The EPMA analysis confirmedsome of the elements attributed to the color of the glass using pXRF. The green and blue-green glasses both contain CuO concentrations above 1%, similar to other green opaque and copper blue glasses analyzed from Amarna (Nicholson 2007). The Cu content in the red opaque glass (E1008B) is similar to thosepreviously analyzed from Amarna and Qantir (Nicholson 2007; Rehren 200). Like the red glass from Qantir, E1008B has a low potash value, 1.92%. The black rod shows that it was clearly colored by both MnO (2.04%) and CuO (1.92%). The concentrations of these two elements are slightly lower than what has been reported in the literature, but still close to the average published values (Nicholson 2007).

VP-SEM-EDS

VP-SEM-EDS analysis was conducted on the opacified glasses (E843A, E843H, E1008C1,

E1008C2, E1008D)to look at differences between the bulk glass composition and the areas of

unmelted/unreacted opacifier (table 7).

The yellow opaque glasses (E843H, E1008C1) were opacified with lead antimonate and the

areas containing the unmelted material were clearly visible using the SEM (fig. 10). The

surrounding bulk glass contained about 0.1-0.6% Sb_2O_3 and about 0.1-0.4% PbO. Though LBA

opaque yellow glasses have been found to contain a little more antimony in the bulk

composition, around 0.6-1.8% (Rehren 2000), lower amounts of Sb_2O_3 have been seen as well

(Nicholson 2007).In the areas where the lead antimonate crystals are visible, the concentration of

PbO and Sb_2O_3 increases- 0.6-1.56% for PbO and as high as 11.5-18% for Sb_2O_3.The yellow

inclusions in the blue-green (E1008D) and opaque green glass (E843A) show a similar trend.

There are low values of both PbO and Sb_2O_3 in the bulk glass (0.1-0.18% and 0.2-0.3%

respectively) and an increase in the concentration of Sb_2O_3 in the areas containing unmelted lead

antimonate (11.5-16.4%).

<Figure 10 here>.

The sources of lead antimonate used in ancient glasses are not well known. Some have proposed

that the source isantiminousargentiferous galena (Mass et al. 2002).The Pb and Sb are a

byproduct of the smelting of galena to extract silver. Once the silver was separated, litharge,

could have been used to create lead antimonate. Not everyone agrees with this theory and others

proposed that the source that lead and antimony were each introduced separately (Nicholson

2007).

The composition of the white opaque glass analyzed (E1008C.2) is also similar to previously analyzed examples from Amarna and other LBA sites (Nicholson 2007). The bulk glass composition of rod (E1000C.2) contains 6.7% CaO, and around 3.19% Sb_2O_3. In the areas with calcium antimonate crystals the composition of the CaO increases slightly to 9.2% and the Sb_2O_3increases to 13.1%. Like with the yellow opacified glass, there are questions as to how these opacified glasses were made. The addition of the mineral stibnite (Sb_2S_3), which is the most common mineral form of antimony, could have been added directly to clear glass, or to the raw materials, for in situ crystallization of the opacifier (Nicholson 2007). Another possibility suggested is that in the eighteenth dynasty (1570-1292BC) Egyptian glassmakers were creating calcium antimonate crystals ex-situ and then adding them to a translucent glass as an opacifier (Lahlil et al. 2010)

Conclusions and Future Work

The analysis of this small group of glass working debris is still on going, but the preliminary results have provided some information on the composition of the glasses and their colorants.The elements detected and their concentrations show that the rods and strips are similar in composition to glass made in Egypt for this time period. The detection of Sn and Pb in the Cu colored glasses, along with the associated elements found in the Co-Cu glasses, point to Egyptian sources. Comparing the results of the analysis of the Penn Museum rods with published analysis from other Amarna glasses thought to have been made at the site, there are similarities in the concentrations of the bulk glass and colorants identified.The results obtained thus far only point to a likely Egyptian origin, with similarities to glasses thought to be made at Amarna, butthe

source of the raw materials used to make the glass and the primary production center at this point cannot be further identified without additional analysis.

Future analysis of these samples is planned with a focus on determining the geographic source of the raw materials to be determined.Trace element analysis has been used to differentiate glasses of Egyptian and Mesopotamian origin by identifying elements associated with the raw materials found in each region. With continued analysis of large volumes of material, it may also be possible to begin to identify chemical signatures for glasses from different sites within Egypt. At the moment this has not been possible due to the similarities in the raw materials across different parts of Egypt, but perhaps future work focusing on isotopic signatures of the silica sources or flux could help to make these distinctions. The next step for these Amarna rods is to identify trace elements via LA-ICPMS to confirm the Egyptian origin of these pieces. (Jackson and Nicholson 2010; Shortland 2012). Isotopic analysis could also be applied as well to this material for further sourcing and characterization of the raw materials (Henderson 2012).

The glass rods and strips selected for this researchwere used as a pilot project and the hope is that the sample set can be expanded to analyze additional material from Amarna in the Penn Museum's collection. In addition to many pieces of glassworking debris, the museum also holds some of the material described in Petrie's publication that could be indicative of glassmaking. These include the quartz pebbles he found with drips of vitreous material on the surface, as well as fragments of cylinders that have glass attached to them. Analysis of these items could reveal glass in a semi-fused or partially melted state providing direct evidence for glassmaking at Amarna and supporting Petrie's interpretations of the material he discovered there. Along with

the continued analysis of the Amarna rods discussed in the paper, future work will also focus on this additional glass production debris in the Penn Museum's collection. Only through the continued analysis of the material Petrie recovered from the glass manufacturing area, interpreted alongside the findings from more recent archaeological excavations and scientific analyses, will we be able to provide a clearer picture of glass production at Amarna and the larger LBA glass industry in Egypt and abroad.

<Insert Table 1>

<Insert Table 2>

<Insert Table 3>

<Insert Table 4>

<Insert Table 5>

<Insert Table 6>

<Insert Table 7>

<u>Materials</u>

EpoFix Resin and Hardener

Struers Inc.

24766 Detroit Rd.

Westlake

Cleveland, OH 44145

(440) 871 0071

www.struers.com

Mastertex Cloths

Metadi Diamond Suspensions (1 and 6 micron)

Buehler Ltd.

41 Waukegan Rd, Lake Bluff, IL 60044

(800) 283-4537

www.buehler.com

Teflon PTFE rods, 1" I.D.

McMaster Carr

9630 Norwalk Blvd.

Santa Fe Springs, CA 90670-2932

(562) 692-5911

www.mcmastercarr.com

microscope and SEM-EDS; the UCLA/Getty Conservation Program for the use of their sampling

and sample preparation equipment and supplies; Eric Schnittke, Assistant Archivist, Penn

Museum; Dr. Barry Kemp, Director, Amarna Project, The McDonald Institute for

Archaeological Research, University of Cambridge; and Dr. Anna Hodgkinson, Freie Universität

Berlin. Finally the authors would like to thank the organizers of the Penn Museum symposium

for accepting this paper and the reviewers for their comments and edits which helped to greatly

improve it.

Author Bios

Vanessa Muros is lecturer and manager of the conservation training labs at the UCLA/Getty

Conservation Program. She received an MS from University College London specializing in the

conservation of archaeological and ethnographic objects. Her areas of interest focus on

archaeological conservation, both in the field and museums, and the technology and deterioration

of metals and glass. vmuros@ucla.edu

Nicole Little is a Physical Scientist at the Smithsonian Institution's Museum Conservation

Institute. She received her B.A. and M.A. in Anthropology from the University of Missouri-

Columbia, focusing on the compositional analysis of Mayan ceramics from northwest Belize.

Her areas of interest include the quantification of heavy metals in bone by ICP-MS and the

identification of corrosion products by XRD. LittleN@si.edu

Yuan Lin received her B.S. in chemistry from UC Berkeley and worked in the R&D lab of Behr

Process Corporation before her Ph.D. studies in the Archaeomaterials Group at UCLA. She

focuses on reverse engineering and provenance of archaeological pigments and glass. She recently completed Ph.D. research at the Université Pierre-et-Marie-Curie and the Laboratoire de Photoniqueet de Nanostructures in France. yuanlin0705@ucla.edu

Patrick Boehnke received a BS in Physics and in Mathematics from Purdue University and a MS in Geochemistry from UCLA. His areas of interest include applying high-spatial resolution isotope and trace element measurements to geochemical, cosmochemical and archeological problems, in particular as measured by secondary ion mass spectrometry. He received his PhD from UCLA this June and is currently a postdoctoral fellow at the University of Chicago. pboehnke@gmail.com

References

Egyptian Section. 2016. University of Pennsylvania Museum of Archaeology and Anthropology. http://www.penn.museum/about-collections/curatorial-sections/egyptian-section/ Accessed September 23, 2016.

Freestone, I.C. 1987. Composition and Microstructure of Early Opaque Red Glass.In Early Vitreous Materials, eds. M. Bimson and I. Freestone, pp. 173-191. London: British Museum Press.

Henderson, J. 2012. Ancient Glass: An Interdisciplinary Exploration. Cambridge: Cambridge University Press.

Hodgkinson, A.K. 2015. Archaeological excavations of a bead workshop in the Main City at Tell el-Amarna. <u>Journal of Glass Studies</u> 57: 279–284.

Kaczmarczyk, A. 1986. The source of cobalt in ancient Egyptian pigments. In <u>Proceedings of the 24th International Archaeometry Symposium</u>, eds. J. S. Olin and M. J. Blackman, pp. 369–76, Washington, DC: Smithsonian Institution,.

Kemp. B.J. 2014. <u>The City of Akhenaten and Nefertiti: Amarna and Its People</u>. London: Thames and Hudson

Jackson, C.M. and P.T. Nicholson. 2010. The Provenance of Some Glass Ingots from the Uluburun Shipwreck. <u>Journal of Archaeological Science</u>. 37: 295-301.

Lahlil S., Biron, I., Cotte, M., Susini, J. and N. Menguy. 2010. Synthesis of Calcium Antimonate Nano-Crystals by the 18th Dynasty Egyptian Glassmakers. <u>Applied Physics A</u> 98: 1-8.

Mass, J.L., Wypiski, M. and R.E. Stone. 2002. Malkata and Lisht Glassmaking Technologies: Towards a Specific Link Between Second Millennium BC Metallurgists and Glassmakers. <u>Archaeometry</u> 44(1):67-82

Moorey, P.R.S. 1999. <u>Ancient Mesopotamian Materials and Industries: The Archaeological Evidence</u>. Winona Lake, IN: Eisenbrauns.

National Institute of Standards and Technology. 2012. <u>Standard Reference Material 612</u> <u>Certificate of Analysis.</u> Trace Elements in Glass.

Nicholson, P.T. 2007. <u>Brilliant Things for Akhenaten: The Production of Glass, Vitreous</u> <u>Materials and Pottery at Amarna Site O45.1.</u> Excavation Memoirs, Egyptian Exploration Society, Book 80. Oxford: Oxbow Books Ltd.

Nikita, K. and J. Henderson. 2006. Glass Analyses from Mycenaean Thebes and Elateia: Compositional Evidence for a Mycenaean Glass Industry.<u>Journal of Glass Studies</u> 48: 71-120.

Online Collection. 2016. University of Pennsylvania Museum of Archaeology and Anthropology. http://www.penn.museum/collections/ Accessed September 23, 2016.

Petrie. W.M.F. 1894. <u>Tell el-Amarna</u>. London: Methuen and Co.

Rehren, T. 2000. New Aspects of Ancient Egyptian Glassmaking. <u>Journal of Glass Studies</u>. 42: 13-24.

Shortland, A. 2012.<u>Lapis Lazuli from the Kiln: Glass and Glassmaking in the Late Bronze Age</u>. Leuven, Belgium: Leuven University Press.

Shortland, A.J. and K. Eremin. 2006. Analysis of Second Millennium Glass from Egypt and Mesopotamia, Part 1: New WDS Analyses.Archaeometry. 48(4): 581-603.

Shortland A.J. and M.S. Tite. 2000. Raw Materials of Glass from Amarna and Implications for the Origins of Egyptian Glass.Archaeometry 42(1): 141–51.

Shugar, A. N. 2013. Portable X-ray Fluorescence and Archaeology: Limitations of the instrument and Suggested Methods to Achieve Desired Results.In Archaeological Chemistry VIII, eds. R. Armitage and J. Burton, pp. 173-193, Washington DC: American Chemical Society.

Smirniou, M. and T. Rehren. 2011. Direct Evidence of Primary Glass Production in Late Bronze Age Amarna, Egypt. Archaeometry 53(1): 58-80.

Smirniou, M. and T. Rehren. 2013. Shades of Blue-Cobalt-Copper Coloured Blue Glass from New Kingdom Egypt and the Mycenaean World: A Matter of Production or Colourant source? Journal of Archaeological Science 40: 4731-4743.

Smirniou, M., Rehren, T. Adrymi-Sismani, V., Asderaki, E. and Gratuze, B. 2012. Mycenaean Beads from Kazanaki, Volos: A Further Node in the LBA Glass Network. In Annales du 18e Congrès l' Association Internationale pour l' Histoire du Ver, eds. D. Ignatiadou and A. Antonaras, pp: 11-18, Thessaloniki, Greece: ZITI Publishing.

Turner, W.E.S. 1954, Studies in Ancient Glass and Glassmaking Processes, Part I. Crucibles and Melting Temperatures Employed in Ancient Egypt at About 1370 BC. Journal of the Society of Glass Technology 38: 436-44.

Turner, W.E.S. 1956. Studies in Ancient Glasses and Glassmaking Processes: Part V. Raw Materials and Melting Processes.Journal of the Society of Glass Technology40: 277–300

Vicenzi, E. P., Eggins, S., Wysoczanski, R.., and Logan, A.2002.Microbeam Characterization of Corning Archeological Reference Glasses: New Additions to the Smithsonian Microbeam Standard Collection. Journal of Research of the National Institute of Standards and Technology107: 719-727.

Figure Captions

Figure 1. Map showing the location of sites mentioned in this paper. Map data: ©2016 GeoBasis-DE/BKG (©2009), Google, Inst. Geogr. Nacional, MapaGISrael, ORION-ME

Figure 2. Map of Amarna. Map courtesy of the Amarna Project.

Figure 3. Detail from the general plan of Amarna created by Petrie. This plan marks the areas Petrie excavated, including the palace waste heaps ("PALACE WASTE_HEAP") and an area with many amulet molds ("MOULDS"). Image after Petrie 1894.

Figure 4. Some of the Amarna objects upon acquisition by the Penn Museum. The museum sponsored Petrie's work at Amarna and purchased the finds in 1893. Photo courtesy of the Penn Museum Archives.

Figure 5. In the macroscopic view (left), rod E843H looks a solid yellow opaque color. Microscopic examination of a polished section of the rod shows that it appears to be made of colorless glass with inclusions of lead antimonate (right). Left photo courtesy of the Penn Museum Online Collection.

Figure 6. Rod E1008D is described in the Penn Museum online catalog as green but actually appears to be light blue or a blue-green color. The rod is made from a blue glass with added red opaque glass and yellow inclusions. What role these additional colors play in producing the blue tone is not clear. Left photo courtesy of the Penn Museum Online Collection

Figure 7. Bivariate plot of the net photons counts for the elements Mg and K. The plot shows that the dark blue glasses colored by Co and Cu (E843D, E844G,H, J and M)have a lower ratio of Mg and K, elements that come in with the plant ash, than the glass colored by Cu (E1008D,G,H). However the Mg-K ratio of the Co-Cu glasses is within the range of the other colored glasses analyzed and therefore does not seem to fit the general trend observed of Co glasses having much lower potash but high magnesia.

Figure 8. Bivariate plot of the net photons counts for the elements Al and Mg. Glasses colored by cobalt tend to have higher values of alumina and magnesia than other glasses. Four of the dark

blue Co-Cu glasses (E844G,H, J and M) have the highest Al counts and cluster together at one end of the bivariate plot. A fifth dark blue rod, E843D however, has lower counts of both Al and Mg similar to the ratio seen in other colors, such as two opaque green glasses (E843A and L). E843D did contain cobalt and copper but the colorant may have come from a different source than the other Co-Cu glasses.

Figure 9. Comparison of MgO and K_2O values obtained from the 11 Penn rods analyzed and published values from other LBA glasses. The bivariate plot shows that these values are similar between the Penn Amarna rods and other LBA glass primarily from Egypt and Mesopotamia. The bivariate plot also shows the variability of these elements across LBA glasses, even among those made in the same location.

Figure 10. The areas of lead antimonate were clearly visible on E843H when imaged with the VP-SEM. In all the samples that contained lead antimonate, the opacifier appears as patches of a granular looking material within the smooth bulk glass.

Table 1. Summary of analytical techniques applied to each piece of glass included in this study

Table 2. EPMA-WDS analysis of glass standards Corning A, B, C and NIST 612. The accepted values for the Corning standards are taken from Vicenzi, et al. 2002. The 612 values are taken from the NIST Certificate of analysis (2012).

Table 3. VP-SEM-EDS analysis of glass standards Corning A, B, C and NIST 612. The accepted values for the Corning standards are taken from Vicenzi, et al. 2002. The 612 values are taken from the NIST Certificate of analysis (2012).

Table 4. Results of qualitative pXRF analysis

Table 5. Net photon counts for elements detected using pXRF (15kV/25µA, 1mm Ti filter)

Table 6. Results of EPMA-WDS analysis. Concentrations given as weight percent of oxides (wt %).

Table 7. Results of VP-SEM-EDS analysis of glasses that contained opacifiers comparing bulk glass and areas containing unmelted opacifying materials. Concentrations are given as weight percent of oxides.