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The Analysis of 18th Century Glass Trade Beads from Fort Niagara: Insight into Compositional Variation and Manufacturing Techniques

Aaron N. Shugar and Ariel O’Connor

An assemblage of 445 archaeological glass trade beads excavated from Old Fort Niagara, Youngstown, New York in 2007 were analyzed to determine their manufacturing technology and elemental composition. Analytical techniques included reflected light microscopy, handheld X-ray fluorescence (XRF), and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS). Optical microscopy revealed the manufacturing technology of the beads and uncovered discrepancies between the current method of visual identification for bead type and color and the structures and colors revealed through scientific analysis. Elemental analysis revealed a new turquoise blue bead composition.

Introduction

Glass trade beads were commonly used by Europeans to win Native friendship and to trade for various articles. At Fort Niagara in Western New York, glass and wampum trade beads have been found from both 17th and 18th century contexts. Previous investigations have dealt with the historical and archaeological evidence of the use of wampum at Fort Niagara (Peña 2006). Glass trade beads have been studied thoroughly from various archaeological sites in the north-east (Hancock et al 1994, 1996, 1999, 2000; Karklins 1983; Sempowski et al 2000). Scott (2009) describes the glass beads excavated at Fort Niagara between 1979 and 1991. This paper presents the findings from the scientific analysis of a group of 416 out of 445 18th century glass trade beads excavated from Fort Niagara in 2007.

History of the Site

The history of Fort Niagara spans from Native American pre-contact years through 20th-century military training, and its ideal location at the entrance to the Great Lakes system was cause for contest during the 17th and 18th centuries. The French established the first post at Fort Niagara in 1679 and erected a more permanent structure in 1726, now known as the “French Castle”. Following a 19-day siege during the French & Indian War, the British gained control of the site in 1759. The British remained at the post through the American Revolution but had to yield the site, by treaty, to the United States in 1796. The fort was recaptured by the British in 1813 but was again ceded to the United States in 1815 after the War of 1812. Following this war the site remained a peaceful border post, expanding after the Civil War and serving as a training station for American soldiers in both World Wars. Fort Niagara’s collections include one of the United States’ paramount compilations of original 18th and 19th century military architecture and artifacts. Architectural collections include six 18th century buildings, one of which is the oldest building in North America between the Appalachian Mountains and the Mississippi River, and extensive areas of 18th and 19th century fortifications.
Collection of beads

The glass trade beads investigated in this study were excavated from a location associated with a mid-18th-century French building known today as Structure 408 but labeled on French-era maps as the “officers’ quarters” and British-era maps as the “Command'rs room”. From the varied archaeological finds associated with this structure, it has been suggested that this was the location for the majority of trade (Peña 2006). Initial dating of the glass beads was established based on related ceramic finds. Tin glazed earthenwares with decoration characteristic of 1760 Liverpool production have been found in addition to several creamware ceramics which post-date 1762. This evidence firmly places the glass beads in the second half of the 18th century and more likely in the third quarter of the 18th century (Peña, pers. com. 2008).

Compositional analysis of trade beads has shown distinct variation in chemistry over time (Hancock et al 1994, 1996, 1997). The present analysis and study of these glass trade beads will provide more information concerning their elemental composition and manufacturing technology, help to refine and/or confirm the current dating, and ultimately may provide insight into the complex trade routes that existed in the Northeast during the 18th century.

Initial Classification

Onsite classification of bead type was established using the Kidd Classification System (Kidd and Kidd 1983, Karklins 1985). Archaeologists have focused their attention of studying glass trade beads on typological classifications, recording manufacturing technique, color, decoration, and shape. The established Kidd classification system (1983) has been extended by some (e.g., Karklins, 1985) and has become the norm for classifying trade beads in eastern North America. Certain bead types have become time markers for dating European contact. This classification technique has been used extensively to allow inter and intra site comparisons of beads and has been found useful in establishing dates for contact period archaeological sites. By comparing the bead’s color, shape, visual layering structure, and method of production with illustrated examples, all 445 beads from Fort Niagara were grouped and assigned Kidd numbers. The majority of the beads in this assemblage were un-cored, rounded drawn beads (Kidd type II). There are two wound beads in the collection as well as four tubular beads (Kidd type III). The breakdown of colors is as follows; white (330 beads, 74.2%, Kidd type IIa12), turquoise blue (47 beads, 10.6%, Kidd type IIa37), dark blue (39 beads, 8.8%, Kidd type IIa56), red (11 beads, 2.5%, Kidd type IIa2), black (9 beads, 2%, Kidd type IIa7), green (7 beads, 1.6%, Kidd type IIa27), and clear (2 beads, 0.4%, Kidd type IIa19) (fig. 1). Previous investigations of the chemistry of trade beads excavated in the Northeast have focused on the white (Hancock et al 1997, 1999; Sempowski et al 2000), blue (Hancock et al 1994, 1996, 2000) and red (Sempowski et al 2001) beads. With the majority of beads in this collection being either white or blue, this study will focus on these two colors only.

Several key papers have established beads as time markers based on distinct changes in elemental composition over time. In some cases these compositions can be associated with specific production centers (Hancock et al 1994, 1996; Kenyon et al 1995a; Moreau, J.F. et al., 2002). These elemental changes in composition are found in the colorants and opacifiers, and, in particular, the alkali metals (sodium and potassium). These alkali metals are essential ingredients in glassmaking, serving as a flux, reducing the temperature at which the silica glass former melts.

Based on previous compositional analysis, five separate periods spanning approximately 350 years were established for blue trade beads but these periods have been shown to be similar for all colors. These periods are; 1. Early French regime (1580-1650), 2. Late French regime (1660-1760), 3. Early British regime (1760-1840), 4. Victorian era (1840-1900), and 5. Early 20th century (1900-1930) (Hancock et al 1994). The white trade beads show similar distinctions with slight variations from the established dating of the blue beads. Changes in white bead chemistry can be discerned in the alkalis and opacifiers used over time but with some overlap, for example, the elements used to opacify white glass change from tin (1600-1700), to antimony (1650-1890), to arsenic (1800-1949) (Moreau, J.F. et al 2002).
Analytical Methodology

Cross-section analysis and X-ray fluorescence were both used to investigate manufacturing technology and elemental composition of the beads. In conjunction these techniques offer a more complete picture of the 18th century beads from Fort Niagara.

Cross-Section Analysis

Several beads were selected for cross-section analysis. Beads were mounted in epoxy resin and were ground on successive grit of SiC wet sandpaper (180, 400, 600, and 1200 grit) and polished with diamond paste at six µm, three µm, and one µm. Final polish was done with 0.5 µm alumina suspension. Sectioning and polishing the beads allowed the manufacturing techniques to be determined and indicated if a bead was produced with a cored or un-cored structure. Multiple layers could be identified and corrections made to the visual identification of bead structure and color based on Kidd classification. The beads were then examined and photographed using a Zeiss Axio Imager M1A reflected light microscope and a Hitachi S-4000 scanning electron microscopy (SEM-EDS) run at 15Kv to confirm heterogeneity and elements contributing to color and opacity.

XRF Analysis

Non-destructive handheld X-ray fluorescence (XRF) was used to determine the general elemental composition of each bead providing elemental concentration for Potassium (#19) to Uranium (#92) on the periodic table. The analysis was performed on an Innov-X Classic Alpha 1 Handheld XRF Analyzer run at 35 kV and 7µA for 30sec in soil mode. A stainless steel standard was used every twenty samples to reduce detector drift. In addition, several samples were initially sent to Innov-X for analysis to optimize runtime parameters and ensure better data collection. Although handheld, open-architecture XRF is not an ideal method of analysis for small glass beads based on the method’s inability to measure relevant lighter elements (e.g. Sodium, Potassium and Silicon) reliably, the technique was deemed

![Assemblage of Glass Beads from Fort Niagara](image)

Figure 1. Breakdown of the assemblage of glass beads excavated at Fort Niagara by count and percent.
appropriate for investigating the coloring and opacifying agents used in the beads. In addition, without inter-instrument standardization, the collected data may not be directly relatable to published data of comparable beads using more established techniques of analysis (such as INAA or ICP). There is, however, excellent intra-group correlative data that can be compiled for analysis and the resulting elemental ratios can be compared to alternative techniques. Ultimately, additional chemical characterization should be performed using more traditional methods of analysis to assess the handheld XRF results.

**Results and Discussion**

**Cross-section analysis**

Microscopic examination indicates that the beads are slightly weathered with some surface pitting and have a thin corrosion layer. Examination of the mounted and polished beads clearly indicates the potential for significant misclassification and improper Kidd assignments by visual examination alone. This is based on the ability to identify varying manufacturing techniques and multiple layering structures which are only observable through microscopy. The blue (initial classification of IIa56) and white (initial classification of IIa12) beads both revealed that they are cored with an outer colorless band of glass approximately 0.02 mm thick surrounding the central colored glass matrix (FIG. 2). This was not apparent with visual examination of the whole bead alone.

The cross section of the blue bead showed a fairly homogeneous glass matrix with few small inclusions and seeds. The outer surface displayed a thin layer of corrosion. The cross section of the white bead showed a heterogeneous glass opacified and colored by calcium antimonate as determined by SEM-EDS (FIG. 3). The outer band of clear glass had no detectable calcium antimonate crystals, as confirmed by SEM-EDS.

**XRF Analysis**

Although XRF is a proven technique for acquiring elemental data, two influences can have a negative effect on analysis and the reliability of the resulting data. XRF is a surface sensitive technique and, as such, is susceptible to changes in surface chemistry. Corrosion of glass constitutes a depletion of alkali metals from the glass structure altering the surface composition of the glass. In addition, the beads all appear to be cored with a thin layer of clear glass surrounding the colored core. Although the XRF does provide data for the entire bead, the thin glass layer will have an influence on the resulting data in correspondence with the glass composition. It should only affect the data related to the alkali metals used in the
glass and not the coloring and opacifying agents that are the subject of this investigation.

Blue Beads

Visually, the blue beads from Fort Niagara fall into two major categories; a dark blue and a light turquoise blue. Copper, manganese, and cobalt are metals that can be used to produce varying degrees of blue ranging from turquoise blue and violet blue to dark blue colors in glass (Bamford, 1977). Turquoise blue beads typically have copper as their major colorant, ranging from between a half a percent to over 5%. Manganese in excess of over 1000 ppm may add some violet coloration to glass. Very small concentrations of cobalt are required to alter the color of glass to a deep blue (as low as 200 ppm). In fact, cobalt is such a powerful colorant that it takes as much as 24 times the amount of copper and 13 times the amount of manganese to obtain comparable intensities in color (Bamford, 1977: 63-66). Elemental composition clearly distinguished between the two blue colored beads found at Old Fort Niagara, with cobalt coloring the dark blue beads and copper coloring the majority of the turquoise blue beads.

Dark Blue Beads

The 39 dark blue beads are colored by cobalt with a mean of 516 ppm (Table 1). They have relatively high manganese levels (852 ppm) which may add to the depth of their color. This composition closely matches the one dark blue bead that was analyzed from Ashuapumushuan (Moreau et al 1997) having almost identical levels of manganese, cobalt, copper, tin and antimony. For all the blue beads, in particular the dark blue beads, there is a strong positive correlation between arsenic and cobalt (Fig. 4). This relationship has previously been reported by Hancock et al 2000 in which they suggest the correlation is related to the possible co-sourcing of arsenic and cobalt in the mineral form smaltite. This particular mineral is found in the Harz Mountains of eastern Germany, which are relatively close to Amsterdam and Venice, both known glass trade bead making centers. One variation (from Hancock et al 2000) is an arsenic cobalt atomic ratio of approximately two to one whereas the Fort Niagara data show the exact opposite. This difference may be due to the use of a handheld XRF as opposed to neutron activation analysis as an analytical technique, warranting further investigation.

Turquoise Blue Beads

The turquoise blue beads can be categorized into two groups based on their chemical composition (Table 1). Group one is characterized by low levels of copper (0.98%), and high levels of lead (2.09%). Group two is characterized by very low copper content (273 ppm), relatively high cobalt content (196 ppm) and manganese content (1175 ppm), and exceptionally high antimony content (1.97%).

Previous studies of the chronological changes in the chemistry of turquoise blue beads suggest that the ratios of chlorine to sodium (Cl/Na) and potassium to sodium (K/Na) may be used
Figure 4. Plot of cobalt vs. arsenic showing the positive correlation. The ratio here is approximately 2.5:1 Co:As.

Table 1. Mean composition of white and blue beads.

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<th>Color</th>
<th>Mn</th>
<th>Co</th>
<th>Cu</th>
<th>As</th>
<th>Sn</th>
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<td></td>
<td></td>
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<tr>
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<td>29</td>
<td>73</td>
<td>2196</td>
<td>753</td>
<td>19774</td>
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Table 1. Mean composition of white and blue beads.
in conjunction with changes in colorants and opacifying agents to attribute beads to various time periods and producers (Hancock et al 1994, 1996). Using the handheld XRF we are unable to collect reliable data for sodium, chlorine, and potassium making comparable analyses of the alkalis to previously published reports unfeasible. In addition, with the surface corrosion and depletion of alkalis, the data obtained would not be reliable. For that reason, this study relies on the coloring and opacifying agents for attributions.

The role of arsenic and antimony as opacifiers in glass changed in the 17th and 18th centuries, with both becoming more prominent and replacing tin as the most common opacifiers for all glass. Previous studies of comparable turquoise blue beads have shown that limited levels of antimony (>0.5%) are present in 18th century beads (Kenyon et al 1995b) but most other studies of blue beads (i.e. Hancock et al 1994) show a curious lack, based on historical grounds alone, of both arsenic and antimony in 18th century samples. Fourteen of the 47 turquoise blue beads have over 16,000 ppm of antimony (between 16,357 to 25,195 ppm) and relatively low copper content but significant manganese content ranging from 224 ppm to 1.12 wt% (with a mean of 1175 ppm) (Fig. 5 and 6).

High antimony turquoise blue beads are relatively rare, and only a handful has been found in the Northeast (Hancock, pers. com. 2008; Kenyon et al 1995b). Only 17 beads with high antimony content have been identified from the Early British regime (1760-1840). The sites where these beads were found include Grimsby (1), Ft. Frontenac (1), Petit Macatina (1), Peribonka River (3) and Moose Factory level III (9). Two additional antimony-rich beads, one from Ashuapmushuan and the other from Chicoutimi, have manganese levels from 1300-1900 ppm and lead (1496 ppm) are also present in more substantial levels. The first group of beads is closely comparable to group 3.1 of the Ashuapmushuan site assemblage (Moreau et al 2002) which were dated based on their chemistry to the mid to late 18th century. This date fits nicely with the stratigraphically-related ceramic assemblage found at Fort Niagara. In addition, the chemistry of the first group of white beads matches the previously reported data based on two separate factors. First, a shift occurred in the chemistry of the opacifying agent of white beads from using tin to antimony to arsenic over time (Sempowski et al 2000). By 1655-70 it appears that the transition of opacifying both cored and un-cored beads of all shapes and sizes with antimony instead of tin was initiated. By the last quarter of the 17th century this process was

There are several higher manganese blue beads from the Late French regime at Bead Hill, Molson-Huron period I, Chicoutimi, and Ft Frontenac (manganese levels from 1300-1900 ppm) but these beads do not have substantial amounts of antimony. The replacement of copper by manganese as a colorant is curious and the origin of these beads should be explored in more detail.

White beads

The white beads can be categorized into two groups. The first group (6 beads) has very high levels of lead (24.98%) with low levels of calcium (2.8%). Interestingly, there are fairly high levels of copper in this group (2106 ppm) and traces of antimony (210 ppm) and manganese (163 ppm). These beads containing high levels of lead and low tin have no known comparisons. This may be because the majority of previous analyses were done by INAA which is unable to reliably detect lead. Lead does provide some level of opacity and depth to the glass but has previously not been reported in drawn beads. High lead potash wound beads are found and these may be related to some extent. In any case these six beads should be studied in more detail.

The second group comprises 324 of the 330 white beads and has high concentrations of antimony (2.23%) and calcium (6.67%) with no tin or cobalt. Traces of arsenic (124 ppm) and copper (202 ppm) are present. manganese (1301 ppm) and lead (1496 ppm) are also present in more substantial levels. The first group of beads is closely comparable to group 3.1 of the Ashuapmushuan site assemblage (Moreau et al 2002) which were dated based on their chemistry to the mid to late 18th century. This date fits nicely with the stratigraphically-related ceramic assemblage found at Fort Niagara. In addition, the chemistry of the first group of white beads matches the previously reported data based on two separate factors. First, a shift occurred in the chemistry of the opacifying agent of white beads from using tin to antimony to arsenic over time (Sempowski et al 2000). By 1655-70 it appears that the transition of opacifying both cored and un-cored beads of all shapes and sizes with antimony instead of tin was initiated. By the last quarter of the 17th century this process was
Figure 5. Antimony vs copper in the turquoise blue beads. The high antimony beads have a mean of only 273 ppm copper.

Figure 6. Antimony vs manganese in turquoise blue beads showing the increased concentration of manganese in association with higher antimony.
complete and all beads entering the Northeast were opacified by antimony. Beads opacified by arsenic were introduced in the late 18th century (Hancock et al 1997; Sempowski et al 2000). Second, there appears to be a shift in manufacturing technique moving away from producing solid (un-cored) colored glass, to cored colored glass beads which were made with an opacified core surrounded by clear glass. By the early 18th century, this transition appears complete. There is some evidence from Seneca sites that the Dutch West India Company was likely a commercial supplier for the antimony rich beads in the late 17th century (Sempowski et al 2000). It is quite probable that the same source of glass beads still existed in the mid-to late 18th century.

Conclusions

Cross-section analysis

Cross-section analysis is a valuable tool in determining the manufacturing technology of glass beads. Properly establishing the layered structure will allow for a more accurate placement in the Kidd classification system. For most identifications, visual characterization is sufficient to ascertain the accurate colors and design. Unfortunately, even careful examination under a binocular microscope did not reveal the cored outer colorless glass layer found on the blue and white mounted beads in this study, especially when there is a thin layer of corrosion present. The irreversibility of mounting beads makes this method of analysis impractical for all but a few samples and undesirable for larger or rarer beads. If possible, perhaps a representative bead for each color found at a site could be further investigated to more accurately identify the bead’s production and corrosion depth. These samples could then guide archaeologists in the field in classifying the remainder of the beads excavated.

Interestingly one can overcome some of the adverse effects of the corrosion layer by saturating the bead with ethanol. This saturates the corrosion and provides a more accurate color assessment and better classification and is a feasible option for archaeologists wanting to make more accurate assignments in the field.

Elemental Composition

Analysis of glass trade beads by handheld XRF has many benefits but also has some drawbacks. The technique itself is well proven and provides a quick, sensitive, non-destructive method for the analysis of glass. With its ease of use and portability, it can be used on site to provide archaeologists with instant results. Ultimately this could help direct excavations and save time. Unfortunately handheld XRF is restricted with respect to the identification of alkali metals which have a proven themselves to be invaluable as chronological markers. This inability to collect reliable alkali data limits attempts to identify sources for the origin of the glass. The colorants and opacifiers alone are not always enough to determine manufacturing locales. Fortunately, the resulting data does provide comparable ratios of concentrations for opacifiers and colorants which can be compared to other studies.

The data did prove to have some intriguing results. Cobalt was found to be the colorant for the dark blue beads and a previous correlation between cobalt and arsenic was confirmed. Two compositional groupings were exposed for the turquoise blue beads, the first being a traditional copper-colored blue, the second being a new compositional group containing high antimony and manganese and low copper. An assemblage of 14 beads in this group suggested that they may have arrived as one collection and Fort Niagara may have been the initial port of entry for these beads to be further distributed. Further elemental analysis of these beads should be performed to investigate their alkali metals for a more detailed comparison to other known glasses of the period. The white beads also fell into two groups. The first was a high antimony opacified glass which closely matches known mid- to late-18th-century white glass beads from the region and may well have been produced in Dutch glassmaking centers. The second is a high lead white glass which has no comparisons in the literature.

Accurate descriptions of bead typology are important for comparative purposes between collections and manufacturing sites, and observations made using reflective light microscopy and XRF have indicated that visual examination is not sufficient to accurately
describe certain bead color combinations, especially in the presence of corrosion.

The relative dating of the glass trade beads from Fort Niagara to the third quarter of the 18th century based on ceramic finds seems to fit nicely with the elemental chemistry of the beads. The white beads all fall into the center of the production period of high antimony dating from 1650-1890 and before the introduction of arsenic (1800-1949). The blue beads also fall nicely into the Early British regime (1760-1840). Although this period shows variation in alkali metals, it does indicate an increase in the use of antimony as an opacifier as the beads from Fort Niagara demonstrate. The beads studied here clearly do not fall into the Victorian Era (1840-1900), as they do not contain arsenic which was introduced to replace antimony during this phase. The high levels of manganese found in the Fort Niagara beads also ties in nicely with the Early British regime, since later beads have very low levels of manganese, made from relatively pure raw materials. This firmly confirms the estimated date of the third quarter of the 18th century as the date of the beads’ arrival in Fort Niagara.

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