



THE BEAD FORUM

Newsletter of the Society of Bead Researchers

Issue 56

Spring 2010

The Application of X-Ray Fluorescence (XRF) Spectrometry in the Characterization of Glass Degradation in Beaded African Art

Maria Fusco and Robert J. Speakman

The utility of X-ray fluorescence spectrometry in the study of stable and degraded glass as well as coatings applied to ethnographic costume is discussed. South African Ndebele costume and ceremonial regalia were studied from the collection of the National Museum of African Art, Smithsonian Institution, as part of a larger condition survey of the entire beaded collection. The susceptibility of certain types (i.e., colors) of glass beads was noted as well as the presence of a potentially indigenously applied coating which appeared to interact chemically with unstable glass beads. Potentials and limitations of XRF in glass compositional analyses, coating identification and detection of pesticide residue on ethnographic art are discussed.

In 2009, a study was undertaken of beaded costume and sculpture at the Smithsonian Institution's National Museum of African Art (NMAfA). The project's goal was to document the conservation issues particular to African beaded art as evidenced in one major collection. To our knowledge there has been no large-scale investigation of bead degradation specific to African art. Most conservation-related literature focuses on Native American and western beaded art and costume (e.g., Fenn 1987; Carroll and McHugh 2001; Loughheed 1986; Sirois 1999).

The NMAfA collection is comprised of more than 10,000 objects, over 500 of which are beaded. The study focused exclusively on beaded costume and sculpture, ignoring sparsely beaded objects such as wooden sculptures adorned with bead necklaces. The overall condition of the NMAfA beaded collection was assessed. The stability of glass beads was of particular interest given that beads are known to have problems in other collections. It was a priority to note trends in the susceptibility of certain object types, material combinations, or amongst cultural groups.

Three hundred and forty-four pieces of beaded sculpture and costume from 24 different African

cultures were condition surveyed. Trends in degradation were documented both in the stability of certain component parts and amongst cultural groups. Substrates and stringing mechanisms were generally stable. In contrast, glass degradation posed a distinct problem: 17% of the surveyed glass beaded collection exhibited glass deterioration. Furthermore, it was found that the majority of these deteriorating objects (78%) originated from two African regions — two cultural groups in Cameroon (the Bamum and Mandara Mountain groups) and the Ndebele of South Africa.

Continued on page 3



Figure 1. Ndebele *Mapoto*, a married woman's apron (Photo: Franko Khoury, National Museum of African Art Accession # 83-12-61, Smithsonian Institution).

Message from Our President

As an archaeologist, I hear certain questions over and over again about glass beads from archaeological sites: Where was the bead made? How old is it and how was it made? These questions are universal for those of us who study beads and they also pertain to beads and beadwork on objects and to beads that were made recently. These are often the first questions for those of us who are interested in the history of beads. One approach to answering these questions is to look at the chemical composition of a bead. The comparative chemical study of many beads can provide information on the origin, date, manufacture, and preservation of glass beads. Glass, in general, is made by melting sand, flux, colorants, and opacifiers, each of which has distinct chemical properties. Chemical studies were once conducted primarily via Neutron Activation Analysis that required making a glass bead temporarily radioactive. In the last few years, Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry has become a commonly used technique. In this approach, a laser vaporizes a barely visible, pin-sized sample on the surface of the glass. The composition of the vaporized glass is then read with a mass spectrometer. More recently, a number of individuals have begun using portable x-ray fluorescence (XRF) instruments to analyze the x-rays that are bounced off of the glass. An XRF study on beads from ethnographic objects is in this issue of *The Bead Forum*. Each technique has its strengths and limitations and they differ in precision and in the number of chemical elements that can be detected. As these techniques become more common it is likely that there will be major strides in understanding glass bead chemical compositions. Based on bead chemistry we may be able to study many aspects of beads, including the chemical signature of manufacture in a particular geographic area, and we may find that the chemical composition of beads varies temporally and can be used to help determine the age of beads.

Sincerely,
— Bill Billeck, President

Officers and Others

President: Bill Billeck, Department of Anthropology, National Museum of Natural History, Smithsonian Institution, BILLECKB@si.edu

Journal Editor: Karlis Karklins, former Head of Material Culture Research, Parks Canada, karlis4444@gmail.com

Secretary/Treasurer: Alice Scherer, Founder, Center for the Study of Beadwork, alice@europa.com

Bead Forum Editor: Laurie Burgess, Associate Chair, Department of Anthropology, National Museum of Natural History, Smithsonian Institution, BURGESSL@si.edu

Bead Forum Design, Layout and Mailing: Alice Scherer

Journal Layout and Printing Preparation: David Weisel

Finance Committee: Joan Eppen and Lois Rose Rose

Editorial Advisory Committee: Laurie Burgess (chair), Christopher DeCorse, and Marvin T. Smith

Publications Committee: Karlis Karklins (chair), Alice Scherer, and Margret Carey

Society of Bead Researchers, PO Box 13719, Portland, OR 97213
<http://www.beadresearch.org>

Table of Contents

The Application of X-Ray Fluorescence (XRF) Spectrometry in the Characterization of Glass Degradation in Beaded African Art..... 1

Society News.....3

Treasurer’s Summary Report for 2009.....4

Proposed 2010 Budget.....5

Exhibitions/Conferences....13

Selected Publications.....13

Article Submission Guidelines.....14



Society News

SBR Annual Business Meeting Minutes - January 2010

Annual business meeting notes will be published in the Autumn 2010 *Bead Forum* since a formal meeting was not held at the January Society for Historical Archaeology conference held at Amelia Island, Florida. The board will hold a telephone conference call or email annual meeting some time this summer.



SBR Journal editor Karlis Karklins has a new email address: karlis4444@gmail.com.



Also, please note the Society has a new website and new web address at www.beadresearch.org. Please visit our new website and let us know what you think.



For those of you who still receive the hardcopy version of this newsletter, please consider switching to the electronic version instead. This will allow you to receive the newsletter in color rather than black and white. Plus, in the electronic version, the images can be enlarged to get a better sense of the image details. If you would like to receive the newsletter electronically, contact alice@europa.com.



William Billeck's term as SBR president ends on December 31, 2010. He has agreed to run for a second term. If you are interested in running or would like to submit a nomination, please contact Karlis Karklins (karlis4444@gmail.com). The nominee must be a member of the Society in good standing. The term for the position is three years. Ballots for the presidential election will be mailed with the fall *Bead Forum*.

Continued from page 1

For this paper, elemental analysis using X-ray fluorescence (XRF) spectrometry on a study set of eleven Ndebele objects at the Smithsonian Institution's Museum Conservation Institute in Suitland, Maryland, is described. Information presented here relates to the potential and limitations of XRF spectrometry in the study of deteriorated glass trade beads, particularly in their identification (e.g., type of glass, presence of additives) and the interaction of degradation products with an organic coating, identified on the beads as fatty acids by Fourier transform infrared (FTIR) spectroscopy.

Overview of Glass Composition and Degradation

Historic glass is known to be susceptible to degradation (Clark, Pantano and Hench 1979; Davison and Newton 2003; Koob 2006; Römich 1999). Historic glass has an amorphous silica (SiO₂) structure. Each silicon atom is surrounded by four oxygen atoms, which forms the lattice network. This lattice is interrupted by the inclusion of alkali, alkaline earth, or lead oxide modifiers, i.e., fluxes, which are added to lower silica's melting point to a workable range. The physical inclusion of these oxides weakens the silica lattice.

For a deteriorating alkali glass object, the surface is alkali flux poor and silica rich. Alkali ions (e.g.,

sodium, potassium) are hygroscopic, that is they have a high affinity for water (in both vapor and liquid form) and prefer to migrate out of the glass matrix and dissolve into an aqueous solution on the surface of the glass, forming liquid droplets (hence the term "weeping glass"). The migration of the alkali flux out of the glass is accelerated in an environment with high relative humidity. Since this is an ion exchange process, the alkali ions are replaced by hydrogen ions in the silica lattice. The replacement of larger alkali metal ions with smaller hydrogen ions causes the surface to contract and weaken. Cracking and pitting of the upper surface layer exposes more glass to moisture, continuing the deterioration process. Once the alkali ions leave the glass matrix, they can react with atmospheric pollutants to form salts on the glass surface such as carbonates, formates, sulfates, chlorides, acetates and nitrates (Kunicki-Goldfinger 2008; Sirois 1999). To prevent the alkali ion migration, a stabilizer can be added; often it is lime (CaO). However, the effectiveness of the stabilizer is dependent on both the concentration of the stabilizer and the alkali flux; the stabilizer is ineffective if its concentration is too low (<4%) or if the alkali oxide concentration in the glass is too high (>20%) (Sirois 1999).

Continued on page 6

SBR Treasurer's Summary Report for 2009

Opening balance as of January 1, 2009		\$37,086.04
INCOME		\$ 8,026.40
Annual dues		
Individual-North America	1,470.00	
Individual-Overseas	450.00	
Sustaining	180.00	
Patron	150.00	2,250.00
Publication Sales		
Journal	4,856.45	
Newsletter	219.00	5,075.45
Investment Income		
Interest Wells Fargo Money Market Acct.		24.02
Contributions and Donations		17.50
Miscellaneous		
Prepaid postage, Pay Pal Fees, Credits, Reimbursements		659.43
EXPENSES		\$9,811.80
Journal Production		
Image Rental ROM (one time fee)	66.00	
Layout	779.40	
Printing	5,386.49	6,231.89
Newsletter Production (2 issues)		
Printing		188.95
Postage/Shipping		
Journal	913.48	
Newsletter	123.20	
General orders	526.70	1,563.38
Website Domain and Hosting		59.07
Office Expenses (stationery, supplies, long distance)		
Secretary/Treasurer	159.74	
Journal office expenses	25.83	185.57
Miscellaneous		
SHA Conference Book Room Table Fee	300.00	
Oregon Business filing fees	60.00	
Bank, PayPal charges, and refunds	222.94	
Donation to Bead Museum	1,000.00	1,582.94
Closing balance as of December 31, 2009		\$35,300.64

— Respectfully submitted, Alice Scherer, Secretary/Treasurer (March 31, 2010)

Proposed SBR Budget for 2010

Opening Balance as of January 1, 2010			\$35,300.64
INCOME			\$8,900.00
Annual Dues			
Individual-North America	1,500		
Individual-Overseas	500		
Sustaining	200		
Patron	300		
Benefactor	300	2,800	
Publication Sales			
Journal	5,000		
Newsletter	300	5,300	
Investment Income			100
Contributions and Grants			200
Prepaid Postage and PayPal fees			450
EXPENSES			\$9,275.00
Journal Production (1 Issue)			
Layout	750		
Printing	5,400	6,150	
Newsletter Production (2 issues)			
Printing			190
Website domain and hosting			75
Postage/Shipping			
Journal	920		
Newsletter	125		
General order shipping	600	1,645	
Office Expenses (stationery, supplies)			
Secretary/Treasurer	200		
Journal Editor	400		
Newsletter Editor	30	630	
Miscellaneous			
2010 SHA Conf. Book Room Table Fee	300		
Bank, PayPal charges, refunds	225		
Oregon Business filing fees	60	585	
Anticipated Balance as of December 31, 2010			\$34,925.64

Respectfully submitted, Alice Scherer, Secretary/Treasurer (March 31, 2010)

Continued from page 3

Degrading glass beads in particular have been studied with a focus on Native American and western costume collections. In these studies, classic glass degradation mechanisms were identified, such as the loss of flux components manifested in chemically depleted subsurface layers and physically weakened surface layers (Sirois 1999). Salts also formed on the glass surface (e.g., potassium and sodium carbonates, sulfates and chlorides) (Lougheed 1986; Sirois 1999). Surface salts were found to react further with dressings or tannins in the leather to form potassium fatty acid salts (soaps) on leather-bound Native American beadwork (Fenn 1987).

Although studies of the degradation of glass beaded objects are predominantly based on Native American and western costume collections, we expect African beaded objects to undergo similar deterioration processes described above. One reason is that even though African cultural groups are distinct and geographically distant from Native American and western groups, beginning in the 19th and early 20th centuries when there was a great deal of exploration and colonization, it is highly probable that 1) glass beads were obtained from the same European (e.g., Carey 1986; Labelle 2005; Northern 1975), and/or Asian (e.g., Burgess and Dussubieux 2007; Ross 1990) manufacture and distribution centers that supplied beads to the Americas, or (2) that glass beads used in African beaded art (and/or manufactured in Africa) were produced using similar recipes to those used elsewhere and hence subject to the similar deterioration processes.

However, even if the beads from an African cultural group are similar in composition or imported from the same sources as the Native American group and/or the west, the materials in contact with the beads could be different and unique to Africa. The substrates and stringing mechanisms are often, but not always, indigenously or locally produced and may introduce culturally-specific pigments, dressings and other applied materials that affect the degradation process of the beads. The significance of the object and/or its use may introduce unique materials as well. Thus, information gathered on glass degradation of Native American or western beaded art may not necessarily apply to African beaded art.

Study Set: Ndebele Art Objects

Degradation of the glass beads was a distinct problem amongst the Ndebele objects in the NMAfA collection; almost one-third of those studied displayed

bead degradation to some degree. These objects included mid-to-late twentieth-century costume, jewelry and ceremonial regalia (Figure 1). Fields of multi-colored opaque and translucent glass beads covered the majority of leather and cotton substrates; jewelry was without substrate.



Figure 2. Cotton canvas substrate bearing a thin, crystalline coating (Photo: Mel Wachowiak and Maria Fusco, Museum Conservation Institute, Smithsonian Institution).

This paper focuses on analysis of the Ndebele objects that have degrading glass beads, some that appeared to be coated. A greasy coating was found on many pieces of costume, jewelry and ceremonial regalia (e.g., women's pelvic aprons, children's breast-plates, pendants and a ceremonial staff). The coating did not appear to be associated with a leather dressing given that it was found on cotton canvas and cotton knit objects as well as beaded jewelry with no substrate (Figure 2 and Figure 3). This coating was not only found on the substrates but also appeared to have been applied directly to the beads.



Figure 3. Leather substrate bearing a thin, crystalline coating (Photo: Mel Wachowiak and Maria Fusco, Museum Conservation Institute, Smithsonian Institution).



Figure 4. Stable glass bearing a thin “sugary” coating. Qualitative glass compositional analyses were undertaken with μ -XRF (Photo: Mel Wachowiak and Maria Fusco, Museum Conservation Institute, Smithsonian Institution).

As is often the case with beaded art, certain colors of glass seemed more susceptible to degradation than others. Furthermore, the degrading beads appeared to have chemically interacted with the greasy coating. Stable beads were physically intact and bore a coating that was transparent and thin, like a sugary glaze (Figure 4). The extent of the degraded beads ranged from moderate to severe cracking to complete dissolution. On the surface of most degrading beads, coatings were present that had thickened and yellowed or become opaque (Figure 5 and Figure 6). For the purposes of this discussion, these categories can be drawn:

1) Stable glass beads bearing a thin, transparent coating



Figure 5. Unstable glass bearing a thickened, yellow coating. Qualitative glass compositional analyses and identification of degradation products were undertaken with μ -XRF (Photo: Mel Wachowiak and Maria Fusco, Museum Conservation Institute, Smithsonian Institution).



Figure 6. Unstable glass bearing an engulfing, opaque coating. Qualitative glass compositional analyses and identification of degradation products were undertaken with μ -XRF (Photo: Mel Wachowiak and Maria Fusco, Museum Conservation Institute, Smithsonian Institution).

- a. Opaque blue, black and red glass
- b. Translucent green glass
- 2) Unstable glass beads bearing a thickened and opaque or yellowed coating
 - a. White opaque glass
 - b. Pink opaque glass
 - c. Orange translucent glass
 - d. Red translucent glass

Four items were of principal interest in this study: 1) was a classic glass degradation mechanism occurring 2) were the coating and the degrading glass chemically interacting 3) why was some glass stable and others unstable and 4) what was the coating?

X-Ray Fluorescence Spectrometry

Obtaining information on the glass composition as well as the chemical composition of the coating was key in resolving these research questions. Two techniques that could have provided elemental composition, including low atomic weight elements, are scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) and laser ablation-inductively coupled-mass spectrometry (LA-ICP-MS). However, both SEM-EDS and LA-ICP-MS would require destructive sampling of the objects since the art objects were too large (on average 60 x 50 cm) to fit in the SEM-EDS chamber and LA-ICP-MS would require the destruction of a small sample. Removal of intact beads was not an option. Thus, it was determined that analysis of the beads on the art objects could only be performed *in situ*.

X-ray fluorescence (XRF) spectrometry, a widely used and versatile technique, is well suited for *in situ*, non-invasive elemental analysis. Although it is difficult or impossible to accurately measure by XRF many of the low atomic weight elements (e.g., Na, Mg, Al, Si) that are easily quantified by SEM-EDS, XRF is better than SEM for measurement of many of the higher atomic weights elements (e.g., Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Sr, Zr, etc.). Consequently, it was believed that the XRF spectrometry could be used to address or at least shed light on this particular study without destructive sampling of the beads.

An XRF spectrometer uses primary radiation from an X-ray tube or radioactive source to excite secondary emissions (i.e., the *fluorescence*) from a sample. The energy of the emitted X-rays is characteristic for each element. This technique can be used for qualitative assessment of complex mixtures. The intensity of the characteristic X-ray peak is related to the concentration of the corresponding element in the sample. After appropriate calibration with standards, quantitative analysis of samples for many elements can be made. Limit of detection, depending on the given element and sample matrix, can be as low as a few parts-per-million (ppm). Typically, XRF spectrometry can simultaneously analyze elements with atomic numbers of 11 (sodium) and higher.

The instrument used for analysis of the beads was Bruker AXS ARTAX 800 micro-XRF spectrometer. The instrument is tripod-mounted and the X-ray tube and detector are mounted on an extended "arm" that allow all portions of the object to be accessed with no disruption to the object. All analyses were non-destructive and non-invasive (e.g., non-contact with the object) to the object. The Bruker micro-XRF is equipped with a molybdenum target poly-capillary lens. The X-ray tube has ca. 80 μm spatial resolution. The X-ray detector is a silicon drift detector with a 10 mm^2 active area and energy resolution of ca. 142 eV for the Mn $K\alpha$ at 100 kcps. Each area was analyzed at 50 kV and 600 μA for a live-time count of 30 seconds. As discussed above, XRF can measure higher atomic weight elements. As such, the Bruker micro-XRF could measure elements in the glass and the surface coatings. Such analyses have potential to contribute to an understanding of the glass composition in stable and unstable beads and the chemical composition of the surface coating. As these analyses progressed, additional applications of the XRF became apparent. The

discussion that follows will focus on the XRF's utility in these three areas which contributed to resolution of the research questions core to the project.

Limitations and advantages of *in situ* micro-XRF analysis of glass beads

Micro-XRF spectrometry has many applications in the study of glass in general and glass beads on ethnographic objects in particular. XRF is a surface analytical technique. As such, analytical results are often qualitative since the density of a sample's matrix affects the absorption of X-rays of the photon that are emitted. The generation of quantitative data, such as percent weight compositions of component elements, requires calibration of the spectrometer with matrix-matched standards, i.e., reference materials similar to the sample in both physical geometry and elemental composition. Although glass standards are readily available for creating empirical calibrations, it is much more difficult to obtain (or manufacture) standards that could be used to quantify data for the coated areas of the objects. Within the scope of this study, obtaining or making appropriate reference standards was not possible, thus only qualitative data are reported.

Another disadvantage to XRF is its limits of detection for lower mass elements. To be detectable, elements must be high enough in atomic weight and in concentration for that given element in that specific matrix. The measurement of important glass components such as sodium and magnesium (low atomic weight elements) is possible when the sample is under vacuum or the area between the sample and the X-ray detector are purged with helium. However, even when it is possible to measure sodium and magnesium, the detection limits and analytical precision for these elements is less than optimal. In the case of the Ndebele objects analyzed, the identification of sodium (present in soda glass) cannot be confirmed by XRF, but given that sodium occurs almost without exception in all man-made glass, it is safe to assume sodium is present in the Ndebele beads.

Despite the limitation of XRF for measuring some elements, there are still many advantages to this non-destructive technique that outweigh other analytical approaches. Often elemental identification and qualitative data are enough to answer most research queries. By looking at the counts at a specific X-ray energy associated to the element of interest, concentrations can be categorized as a major, minor or trace amount. For unstable or deteriorating glass,

this information can be enough to identify important components of the glass, such as what flux material was used. In addition to flux, XRF can also detect the presence of additives such as inorganic colorants, colorant modifiers or enhancers and fining agents (added to reduce bubbles in the molten mix). XRF can also identify most high atomic weight elements in degradation products on the surface of glass or indigenous or museum treatment coatings when such matter can be sampled. For all applications, XRF provides information on high atomic weight elements present which aids in predicting a sample's identity at a compound level.

The materials identification provided by XRF is useful not only for art historical or conservation research, but also can identify health and safety issues related to a given ethnographic object. As ethnographic art is often composed of mixed organic materials attractive to pests, they often have been treated with pesticides, many of which are toxic heavy metals that can be harmful to those who handle the contaminated objects. Documentation of pesticide treatment is often scarce for a particular object. XRF spectrometry can be employed to identify the presence of heavy metal-containing pesticides (e.g. mercury, arsenic and lead). With this information, the object can be identified as

contaminated and require proper precautions to be taken (warning signs, appropriate personal protective equipment). A limitation to the use of XRF spectrometry in the identification of pesticides is it is useful only in detecting heavy metal-containing pesticides, not organic pesticides such as naphthalene and dichlorodiphenyltrichloroethane (DDT). The absence of heavy metals does not mean the object is free of harmful organic pesticides.

XRF Results of 11 Ndebele Art Objects

Qualitative Glass Composition Analyses

XRF analysis proved useful in determining the glass type of eleven representative Ndebele objects. This study set represented an array of object types and production period. Between twelve and fifty beads on each object were analyzed for glass composition and findings were very consistent for all objects. Quantitative compositional analyses were not possible as comparative glass standards were not available.

Translucent glass (green, red and orange) was determined to be alkali glass, due to the absence of other elements related to flux materials that could be detected with this XRF setup (e.g., lead). Since it was not possible to measure sodium, it was not possible

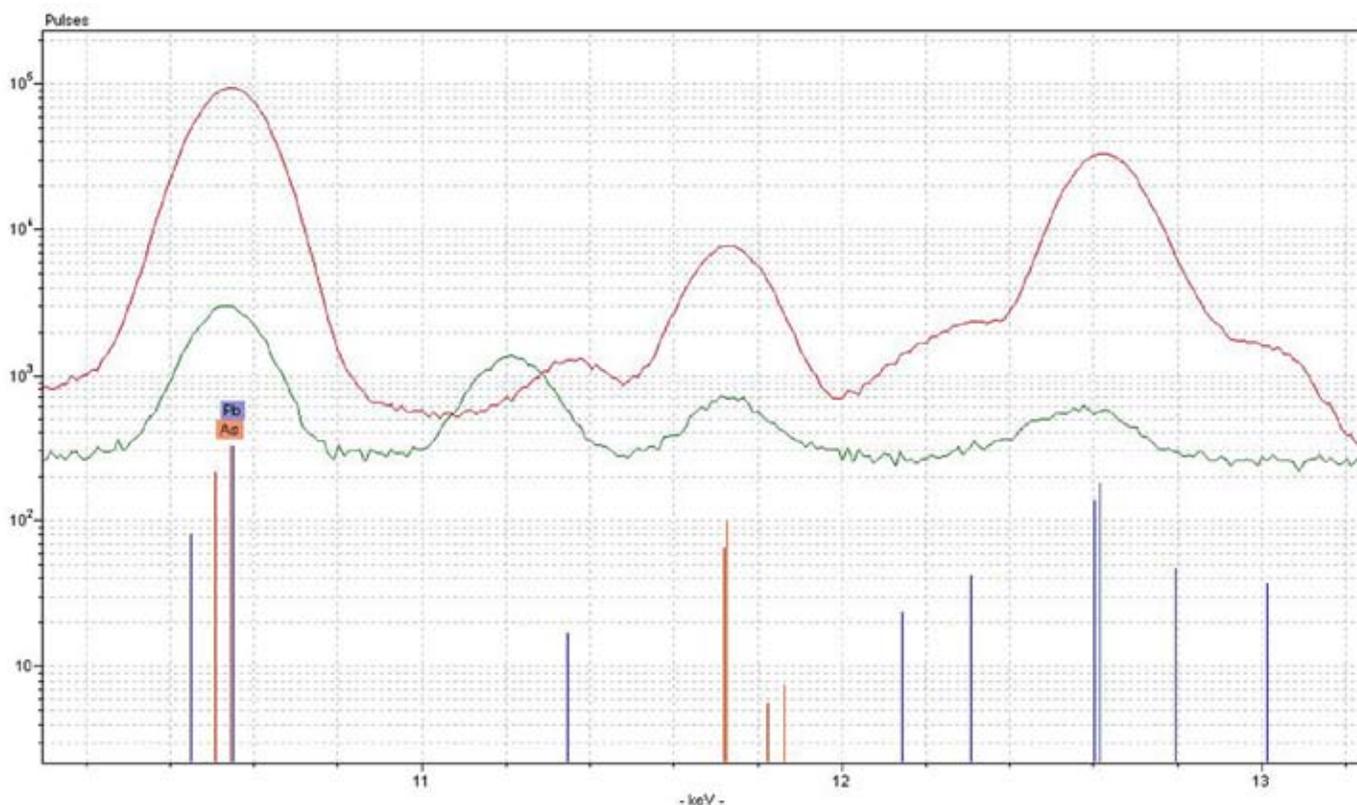


Figure 7. XRF spectra comparing composition of opaque pink (upper red spectra) and red translucent (lower green spectra) glass beads, highlighting lead levels indicated by the L-Beta lead peaks at 12.61 keV. Opaque pink glass registers 586,917 counts (pulses); the red translucent glass registers only 6847 counts.

to confirm if the glass was soda or potash glass. XRF results indicated that the opaque white, pink and blue glasses studied were lead glass. At first, these findings were revisited as the presence of heavy elements such as lead may prevent x-rays of lighter weight elements from reaching the X-ray detector, skewing the results so that it appeared there was more lead in the bead than there actually was. However, this phenomenon was disregarded after comparing the XRF lead peaks for these beads, often 70 times higher than that of other opaque and translucent glass studied (Figure 7). The presence of alkali glass and lead glass is consistent with other studies. In the literature most often consulted by ethnographic conservators, trade beads are spoken of as being strictly soda or potash glass and broader consultations in the archaeological and historical research literature reveal that lead glass trade beads were also in historic use (Burgess and Dussubieux 2007; Ross 1990).

XRF was also very useful in detecting inorganic elements likely added in oxide form as colorants, fining agents or colorant modifiers. Titanium was present in most of the glass beads analyzed; its use was likely to bring out or slightly modify the colorants present in the glass (Weyl 1959). Colorants for the different glass beads were consistent despite the difference in object type and production period. Cobalt was used as the colorant in blue opaque glass, manganese possibly combined with copper in black glass, cadmium and selenium in red and orange translucent glass, and chromium and copper in green translucent glass.

The colorant for the white and the pink glass could not be identified but both glasses shared comparably high levels of arsenic as compared to other glass. Arsenic is often added as a fining agent to make the molten mix less bubbly, and results in a glass that is smoother in appearance. Arsenic is also used to eliminate colored iron impurities in source quartz and as a color stabilizer in the production of pink glass colored with selenium. Here its function is as an oxygen buffer in the furnace since slight fluctuations in oxygen levels could alter glass color especially when cullet is used (Weyl 1959).

Red and orange translucent glass had high zinc levels as compared to opaque and other translucent glass. Zinc is often added not just to impart brilliance to glass but also combined in high concentrations with selenium and cadmium sulfide to produce a range of oranges and reds (Weyl 1959). These findings were of

particular interest as the presence of these glass additives correlated with the stability of the glass. Details of this aspect of the study will be published at a later date.

Analysis of Coating Found on Glass Beads

Given the generally accepted understanding of glass degradation mechanisms, it was likely that the unstable glass beads would have alkali salts on their surface (Clark, Pantano and Hench 1979; Davison and Newton 2003; Koob 2006; Römich 1999). Fourier transform infrared spectroscopy (FTIR) analyses of removed samples of the coating on the degraded glass indicated they were pure salts, more specifically, fatty acid salts. Complementary XRF analyses detected the presence of potassium, calcium, lead and zinc in these coatings. This indicated the fatty acid was chemically combined with potassium, calcium, lead or zinc, forming potassium, calcium, lead or zinc fatty acid salts on the glass surface (Figure 8). Glass compositional analyses confirmed that potassium, calcium, lead and zinc were all components of the underlying glass, supporting understood degradation mechanisms whereby glass components migrate to the surface.

Identification of Heavy Metal Pesticides using XRF Spectrometry

XRF proved useful in assessing health and safety threats presented by these Ndebele objects. While the objects had not been treated with inorganic or organic pesticides to our knowledge, their previous treatment with such chemicals was quite possible. Leather and cotton substrates of all study objects were analyzed at several points. No arsenic, mercury or lead was detected in any of the objects, thus no heavy metal pesticides were used, although the presence of organic pesticides cannot be ruled out.

Conclusion

As noted previously, four matters were of principal interest in this study: 1) was a classic glass degradation mechanism occurring 2) were the coating and the degrading glass chemically interacting 3) why was some glass stable and others unstable and 4) what was the coating? XRF analyses proved useful in providing data which resolved certain research queries and partially resolved others.

An understanding of the composition of these glass beads was achieved which shed light on the greater susceptibility of certain glass. While exact weight percentages of each component oxide were not obtained, qualitative analyses were enough to indicate the type of glass present – either lead or alkali glass.

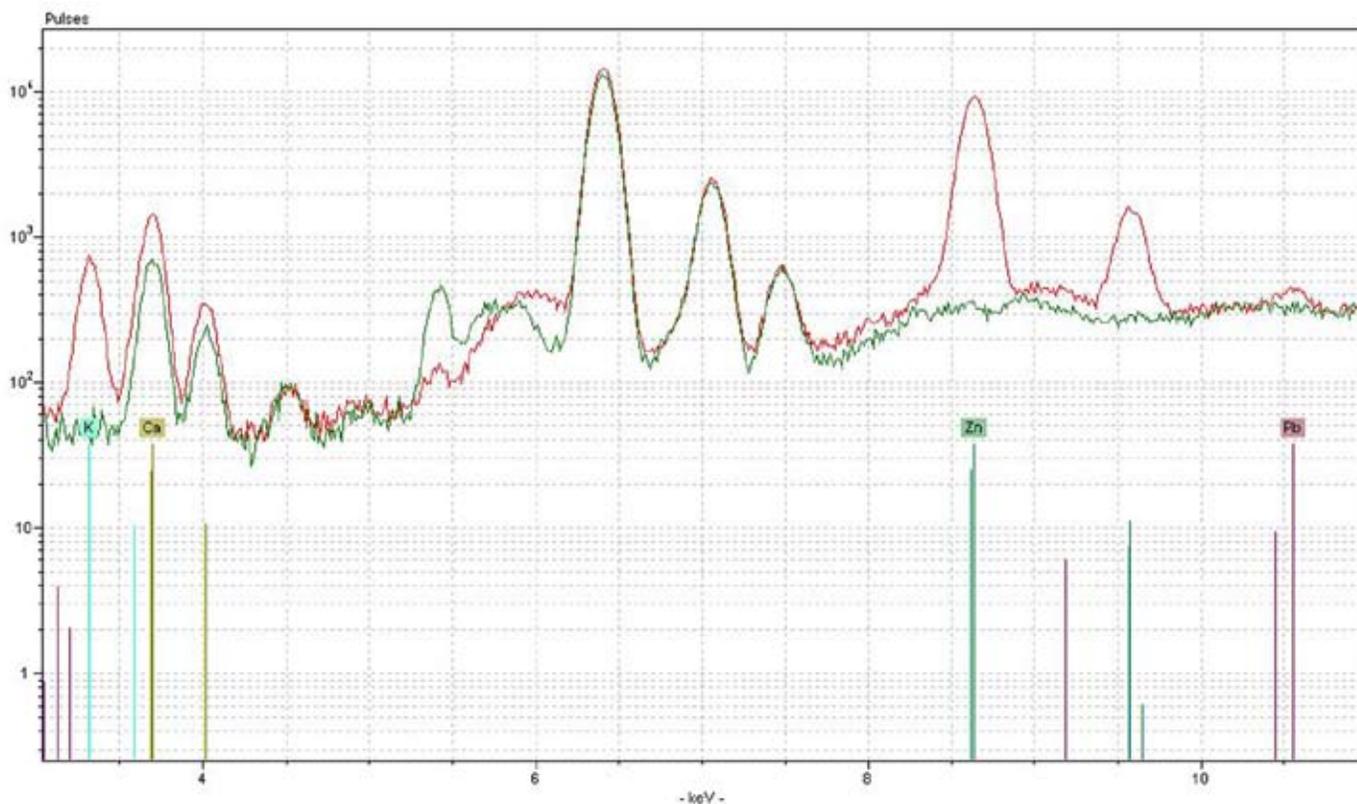


Figure 8. XRF spectra showing analysis of greasy coating removed from the surface of a degrading pink bead. Upper red spectra is the reading of the coating, the lower green spectra is the reading of the foil substrate on which the sample is collected. Areas where the upper red peaks (coating) rise above the green peaks (foil) show the presence of these elements in the coating. Here potassium, zinc and perhaps a little lead are detected within the greasy coating.

Information was obtained on colorants and other additives used; the presence of these additives seemed to correlate with the stability of the glass, which will be described in a publication at a later date.

XRF spectrometry was also a good complementary technique with FTIR spectroscopy in characterizing the interaction of the greasy coating with the degrading glass surface. FTIR analysis provided the organic component (fatty acid) and the XRF analysis provided the cation metal that is bound to the fatty acid. These XRF analyses helped resolve the other three research questions: identification of the greasy coating, indication of whether a classic glass degradation mechanism was underway, and indication of whether the glass and the coating were chemically interacting.

Finally, XRF was useful in ruling out toxic heavy metals as a health and safety concern for these objects. This was not originally a central research question but was useful information to obtain on behalf of these researchers and the NMAfA.

Acknowledgements

Financial support for this study was generously provided by the Samuel H. Kress Foundation and the National Museum of African Art, Smithsonian Insti-

tution. Advisement, analysis and image procurement were kindly provided by Stephen P. Mellor, Stephanie Hornbeck, Bryna Freyer, Janet Stanley, Amy Staples and Franko Khoury of the National Museum of African Art and Jennifer Giaccai, Odile Madden and Mel Wachowiak of the Museum Conservation Institute, Smithsonian Institution. Editorial assistance in the production of this paper was kindly provided by Catherine McLean, Frank Preusser and Charlotte Eng of the Los Angeles County Museum of Art.

References

Burgess, Laurie E., and Laure Dussubieux

2007 Chemical Composition of Late 18th- and 19-Century Glass Beads from Western North America: Clues to Sourcing Beads. *Beads: Journal of the Society of Bead Researchers*, 19:58-73.

Carey, Margaret

1986 *Beads and Beadwork of West and Central Africa*. Shire Ethnography, Princes Risborough.

Carroll, Scott, and Kelly McHugh

2001 Material Characterisation of Glass Disease on Beaded Ethnographic Artefacts from the Collec-

tion of the National Museum of the American Indian. In *Ethnographic Beadwork*, edited by Margot Wright, pp. 27-38. Archetype Publications Ltd., London.

Clark, David, Carlo Pantano, and Larry Hench

1979 *Corrosion of Glass*. Books for Industry and the Glass Industry, Division of Magazines for Industry, Inc., New York.

Davison, Sandra, and Roy Newton

2003 *Conservation and Restoration of Glass*. Butterworth-Heinemann, London.

Fenn, Julia

1987 *Deterioration of Glass Trade Beads in Contact with Skin and Leather or Glass Beads in Soapy Bubble*. ICOM Committee for Conservation: 8th Triennial Meeting, Preprints. 1:195-197. Sydney, Australia

Koob, Stephen

2006 *Conservation and Care of Glass Objects*. Archetype, London.

Kunicki-Goldfinger, Jerzy

2008 Unstable Historic Glass: Symptoms, Causes, Mechanisms and Conservation. *Reviews in Conservation*. 9:47-60.

Labelle, Marie-Louise

2005 *Beads of Life: Eastern and Southern African Beadwork from Canadian Collections*. Mercury Series, Cultural Studies Paper 78. Canadian Museum of Civilization, Ottawa.

Lougheed, Sandra

1986 The Deterioration of Glass Beads on Ethnographic Objects: Symptoms and Conservation. In *Symposium 86. The Care and Preservation of Ethnological Materials*, pp. 109-113. Canadian Conservation Institute, Ottawa.

Northern, Tamara

1985 *The Sign of the Leopard: Beaded Art of Cameroon*. University of Connecticut, Storrs.

Römich, Hannelore

1999 Historic Glass and its Interaction with the Environment. In *The Conservation of Glass and Ceramics: Research, Practice and Training*, edited by Norman H. Tennent, pp. 5-14. James and James, London.

Ross, Lester

1990 Trade Beads from Hudson's Bay Company Fort Vancouver (1829-1860). *Beads: Journal of the Society of Bead Researchers*, 2:29-67.

Sirois, P.J.

1999 The Deterioration of Glass Trade Beads from Canadian Ethnographic and Textile Collections. In *The Conservation of Glass and Ceramics: Research, Practice and Training*, edited by Norman H. Tennent, pp 84-95. James and James, London.

Weyl, Woldemar

1959 *Coloured Glasses*. Dawson's of Pall Mall, London.

MARIA FUSCO

ANDREW W. MELLON CONSERVATION FELLOW

TEXTILE CONSERVATION

LOS ANGELES COUNTY MUSEUM OF ART

5905 WILSHIRE BLVD.

LOS ANGELES, CA 90036

(323) 857-6169

mfusco@lacma.org

ROBERT J. SPEAKMAN

HEAD OF TECHNICAL STUDIES

MUSEUM CONSERVATION INSTITUTE

MUSEUM SUPPORT CENTER

SMITHSONIAN INSTITUTION

4210 SILVER HILL ROAD

SUITLAND, MD 20746

speakmanj@si.edu

Exhibitions and Conferences

Online Exhibits

Between the Beads: Reading African Beadwork is an online exhibit at the Harn Museum of Art at the University of Florida. The exhibit highlights beaded African objects from the museum's collection and from private collections as well: <http://www.harn.ufl.edu/beatwork/>



Made of Thunder, Made of Glass: American Indian Beadwork of the Northeast is online at www.gerrybiron.com and features beaded pouches from eastern North America and many photographs showing Euro-American use of these objects.



Viking Beads

Torben Sode is curating a glass bead exhibit in Denmark at the Moesgaard Museum near Aarhus. The exhibit features both archaeological and ethnographic glass beads and beadwork and will run from May 15 to August 15, 2010.

According to Sode, Ribe, the oldest town in Denmark, is celebrating its 1300th anniversary. The museum in Ribe is exhibiting Viking glass beads that date from 710 to 850. The nearby Viking Centre is reproducing modern versions of Viking beads using small, clay, domed furnaces, which are believed to have been used by the Vikings.

2nd Annual Iroquois Bead Conference

Plans are in the works for the Second Annual Iroquois Bead Conference slated for September 25-26, 2010, to be held at the Seneca Allegany Administration Building in Seneca, New York, in conjunction with the Seneca Iroquois National Museum. Presentations and panel discussions regarding the art and beauty of Iroquois beadwork will fill out the two-day agenda. Activities for the weekend will include viewing a Seneca beadwork exhibit at the museum. For information, contact Dolores Elliot: dolores@stny.rr.com.

Selected Publications/Other Media

Blakney-Bailey, Jane Ann

2008- An Analysis of Seminole Artifacts from the 2009 Paynes Town Site (8AL366), Alachua County, Florida. *Florida Anthropologist* 61(3-4):167-187.

The article describes and illustrates silver and glass beads from a site occupied from 1790-1812.



Bowsher, Julian, and Pat Miller

2009 *The Rose and the Globe: Playhouses of Shakespeare's Bankside, Southwark: excavations 1988-91*, published by Museum of London Archaeology (hardback 172 pp) £26.00.

For a description see: <http://www.shaksper.net/archives/2009/0581.html>. The finds include 250+ beads, primarily glass but also bone, amber and seed pearls dating to the sixteenth and seventeenth centuries.



Shinde, Vasant, Shreekant Jadhav, Prabodh Shirvalkar, Amol Kulkarni, Abhijit Dandekar, Shrikant Ganvir, P.P. Joglekar, Girish Mandke,

Arati Deshpande-Mukherjee, Sushama G. Deo, S.N. Rajagura, M.D. Kajale and Satish Naik.

2008 A Report on the Recent Archaeological Investigations at Junnar, Maharashtra (2005-2007). *Bulletin of the Deccan College Post-Graduate and Research Institute* 66-67:113-159. Deccan College, Pune, India.

Beads made from stone, shell, faience, gold and glass were recovered from archaeological excavations at Junnar, Maharashtra, India.



Shugar, Aaron N., and Aerial O'Connor

2008 The Analysis of 18th-Century Glass Beads from Fort Niagara: Insight into Compositional Variation and Manufacturing Techniques. *Northeast Historical Archaeology* 37:58-68.



Simak, Evelyn, and Carl Dreibelbis

2010 *African Beads: Jewels of a Continent*, Africa Direct, Denver, Colorado.

The Society of Bead Researchers is a non-profit corporation, founded in 1981 to foster research on beads of all materials and periods, and to expedite the dissemination of the resultant knowledge. Membership is open to all persons involved in the study of beads, as well as those interested in keeping abreast of current trends in bead research. The society publishes a semi-annual newsletter, *The Bead Forum*, and an annual journal, *BEADS: Journal of the Society of Bead Researchers*. The society's website address, as of Spring 2010, is <http://www.beadresearch.org>.

Contents of the newsletter include current research news, requests for information, responses to queries, listings of recent publications, conference and symposia announcements, and brief articles on various aspects of bead research. Both historic and prehistoric subject materials are welcome.

The deadline for submissions to the next *Bead Forum* is September 1, 2010. Electronic submissions should be in Word for Windows 6.0 or later with no embedded sub-programs such as "End Notes." References cited should be in *American Antiquity* format (<http://www.saa.org/StyleGuideText/tabid/985/Default.aspx>).

Send electronic or paper submissions to the *Forum* editor:

Laurie Burgess, Associate Chair
Department of Anthropology
National Museum of Natural History
Smithsonian Institution
MRC 112, P.O. Box 37012
Washington, DC 20013-7012
(202) 633-1915
burgessl@si.edu

For back issues of *Beads: Journal of the Society of Bead Researchers*,
or to learn more about us, please visit our website at www.beadresearch.org.

When purchasing five+ copies (need not be the same), a 20% discount may be taken.

Society of Bead Researchers, PO Box 13719, Portland, OR 97213