CHEMICAL COMPOSITION OF 16TH- TO 18TH-CENTURY GLASS BEADS EXCAVATED IN PARIS

Laure Dussubieux and Bernard Gratuze

Dating from the 16th to 18th centuries, 63 glass artifacts (mostly beads) recovered from two sites in Paris, France, were investigated using chemical analysis in an attempt to determine their place of origin. The late-16th-century material from the Jardins du Carrousel consisted of small, monochrome drawn beads with a soda-lime composition. Attributed to the 17th and 18th centuries, the beads recovered at the adjacent site of the Cours Napoléon were more diverse in shape, color, and composition. Although provenance attribution was difficult due to a lack of comparative data, it was possible to identify an increasing variety of glass recipes after the 16th century that revealed a growing interest in glass beads in Europe. In the 17th century and afterwards, greater numbers of glass- and glass-bead production centers were active, quite certainly due to a growing demand for export goods but also due to a more extensive use of beads in France.

INTRODUCTION

Much of what is presently known about glass beads in France from the 16th to 18th centuries is through the work of Kidd (1979) and Francis (1988). Both their publications deal with the broader topic of glass beads in Europe and most of the information they present about France derives from Barrelet (1953) who wrote a comprehensive review of the subject ranging from antiquity to the present. This is also a significant source of information for a more recent book by Bellanger (1988) that focuses on glass vessels but also mentions glass beads, though infrequently.

Turgeon (2001, 2004) provides new insight into this topic by exploring bead importation to northeastern North America from France through the study of post-mortem inventories of Parisian beadmakers dating from the second half of the 16th century to the beginning of the 17th century, coupled with information derived from a contemporaneous collection of beads recovered at the Jardins du Carrousel in Paris. He suggests that glass bead production was significant in France and that beads were exported to North America from France, based on the similarity of the beads found at the Jardins du Carrousel and at sites in northeastern North America. It is, however, important to note that the point of origin of the Jardins du Carrousel beads is unknown and that a French origin is totally hypothetical. Indeed, glass beads recovered in France may have reached their final destination following different paths. One possibility is that they may have been imported from another European country. If previous researchers placed the centers of glass bead production in Holland and Venice, the recent archaeological discovery in London of a glass-bead-producing workshop dating from the mid-17th century (Egan 2007:5) shows that other centers may have existed. Another possibility is that the glass beads may have been manufactured in France from imported semi-finished products (rods for wound beads or tubes for drawn beads). A third possibility is that the rods or tubes and the beads may have both been manufactured in France in separate specialized workshops. A final possibility is that the glass, the rods or tubes, and the beads may have been produced at the same place in France. It is important to note that the production of canes is considered as unlikely as it would have been a Venetian monopoly (Guerrero 2010).

Coupled with archaeological data, it is hoped that the elemental composition of the Parisian glass artifacts will be useful in determining which one of the aforementioned scenarios is the most likely. While the fact that some Italian glassmakers were brought to France (Barrelet 1953) and produced glass according to Italian recipes may create difficulties in differentiating French and foreign productions, the fact that trace element studies have helped to distinguish Venetian and *façon-de-Venise* glassware made at different European locations (De Readt et al. 2001; Šmit et al. 2005) suggests that the same approach may be helpful in the case of the Parisian glass ornaments.

THE BEAD SAMPLES

In an attempt to better understand French glass bead production and trade, this study presents the results of the compositional analysis of 63 beads and glass wasters from two archaeological sites in Paris: the Jardins du Carrousel (end of the 16th century) and the Cours Napoléon (17th-18th centuries). The goal was to define what types of glass composition were available during these periods, their evolution over time, and how they compare with other European glass compositions (Tables 1-2; Plates IVC-IVD). The full description of the corpus of small ornaments, tubes, rods, and wasters found at the two sites will be published separately (Dussubieux n.d.). In many cases in Table 1, Kidd and Kidd (1983) variety numbers could not be assigned to the beads as color nuances were very difficult to distinguish due to the deteriorated condition of the glass.

The Jardins du Carrousel site was excavated in 1989 and 1990. Most of the glass samples came from zone 106 that was used initially as a quarry and then as a dump site from the Renaissance period to modern times. Some beads were also found in zone 102 which was also a quarry and then a dump site. In both cases, the associated ceramics dated to the 16th and 17th centuries (Van Ossel 1998). Fifty-seven artifacts were recorded from this site and were either beads or tubes. The beads, mostly round or roundish, were manufactured using the drawing technique and were quite likely made from the associated tubes. The colors were dark blue, turquoise blue, black, colorless, amber, and greenish. In a few cases it was not possible to determine the color of the glass due to the presence of patination. With the exception of the black glass, the glass was either transparent or translucent.

Situated adjacent to the Jardins du Carrousel, the Cours Napoléon was excavated over a period of 24 months in 1984 and 1985. No excavation report has been published. Formerly living quarters during the 17th and 18th centuries, the site was located where the glass pyramid at the Louvre Museum now stands. The site produced 383 small glass artifacts, mostly in the form of beads and tubes. Other types of artifacts included rods, chain rings, and waste material. The shapes of the beads were quite varied although round and roundish shapes predominated (72%). Other beads were grain shaped, annular, barrel shaped, biconical, truncated bipyramidal, cubical, cornerless cubical, disc shaped, melon shaped, and raspberry shaped. The technique used to manufacture the beads was sometimes difficult to determine, however, drawn, wound, molded, blown, and, more rarely, ground beads are represented. Black beads were the most common followed by turquoise blue, colorless, and dark blue. A significant number of beads were polychrome.

The glass assemblages recorded for the Jardins du Carrousel and the Cours Napoléon sites are rather different in many respects. The modest size of the Jardins du Carrousel assemblage and the poor diversity of the material may be due to its being a dump site. Artifacts ended up there because they were broken or lost. The fact that this site is slightly earlier may also indicate that more diversity in color, shape, and manufacturing techniques appeared later. The Cours Napoléon beads, coming from a domestic context, may have served as personal ornaments or may have been used to decorate furniture, drapes, and other possessions.

As described in Tables 1-2, 14 small glass artifacts were selected for analysis from the Jardins du Carrousel collection and 49 from the Cours Napoléon.

THE ANALYTICAL PROCESS

The beads were analyzed at the Institut de Recherche sur les Archéomatériaux, UMR 5060 CNRS/Université d'Orléans, Centre Ernest-Babelon, using a PQXS-VG Plasma Quad quadrupole ICP-MS connected to a 266 nm UV Microprobe laser system.

In this process, a very small quantity of material is ablated (removed) using the laser. The ablated material is transported by a gas carrier (argon) to the plasma torch where it is dissociated, atomized, and ionized. The ions are then transferred to a quadrupole mass filter. This filter directs ions to the detector with a mass on charge ratio selected by the operator. Each isotope of each element corresponds to a unique mass on charge ratio which allows the identification of the elements present in the sample. The detector records how many ions of each type have traveled through the mass filter. The quantity of each type of ion is directly related to the concentration of the original element in the sample.

The measurements are carried out in peak jump acquisition mode, taking three points per peak. There are two detection modes; the analogue mode is used for major elements and the pulsed mode is used to detect minor and trace elements.

To be able to determine elements with concentrations in the range of ppm and below without leaving a trace on the surface of the sample that is visible to the naked eye, we use the single point analysis mode with a laser beam diameter of 100 μm. The laser operates at a maximum energy of 2 mJ and at a maximum pulse frequency of 10 Hz. A pre-ablation time of 20 s is set in order to first eliminate the transient part of the signal and, second, to be sure that possible surface contamination or corrosion does not affect the results. Measurements on each sample are corrected from the blank.

To improve reproducibility of measurements, the use of an internal standard is required to correct possible instrumental drifts or changes in ablation efficiency. Isotopes Si28 and Si29 were used for internal standardization.

Table 1. Paris Beads Analyzed Using LA-ICP-MS.

Technique	Kidd code	Color	Shape	Dimensions (mm)	Reference number	Comments
Drawn	IIa	Black	Round	L = 12	22.055 (11852) (B)	Faience?
Drawn	IIa	Black	Round	D = 3	12413 (7587)	
Drawn	IIa	Tsp. green	Roundish	D = 4	28551 (17169)	Lead glass
Drawn	IIa	Dark blue	Round	D = 6	3218 (4349)	
Drawn	IIa	Amber	Roundish	D = 7	33335 (19404)	
Drawn	IIa	Turquoise blue	Round	D = 4	3411 (4383)	
Drawn	IIa	Turquoise blue	Round	D = 2.5	3576 (5199)	
Drawn	IIa	Turquoise blue	Round	D = 2.5-3	3592 (5562)A	
Drawn	IIa	Turquoise blue	Round	D = 2.5-3	3593 (5562)B	
Drawn	IIa	Turquoise blue	Round	D = 3	5061 (2525)	
Drawn	IIa	Tsp. yellowish	Round	D = 7.5	6066 (2857)	Fragment, lead glass
Drawn	IIa	Turquoise blue	Roundish	D = 3	9018 (2132)	
Drawn	IIa	Dark blue	Roundish	D = 4	9083 (3654)	
Drawn	IIa	Turquoise blue	Roundish	D = 2-2.5	9380 (11504)A	
Drawn	IIa	Turquoise blue	Roundish	D = 2-2.5	9381 (11504)B	
Drawn	IIa	Turquoise blue	Roundish	D = 3	9596 (15859)	
Drawn	IIa	Turquoise blue	Roundish	L = 6	102.049 (30)A	Fragment
Drawn	IIa	Turquoise blue	Round	L = 6	102.049 (30)C	
Drawn	IIa	Dark blue	Oblate	L = 3	106.001 (59)B	
Drawn	IIb18	Colorless, white	Roundish	L = 7	106.001 (59)C	Colorless with white straight stripes
Drawn	IIa	Dark blue	Round	L = 7	106.001 (59)D	
Drawn	IIa	Black	Roundish	L = 2.5	106.035 (22)A	
Drawn	IIa	Turquoise blue	Roundish	L = 6	106.036 (61)	
Drawn?	IIa?	Dark blue	Grain-shaped	L = 6-7.5	5113 (1389)A	
?	?	Black	Oval	L = 2-3	5113 (1347)	Faience?
Drawn	IIa	Black or dark blue	Roundish	L = 12-16	5113 (1387)	Some tubes from this site may have been used to make these beads
Drawn	IIbb’	Dark blue, blue, white		D = 5-7	2068 (1261) dark blue	Dark blue with spiral blue-on-white stripes
Drawn	IIb18	Colorless, white	Round	D = 7	17498 (18032)	Colorless with straight white stripes; white is mixed lead-alkali glass
Drawn	IIb19	Colorless, white	Oval	D = 7 L = 10	26037 (15067)	Colorless with straight white stripes
Drawn	IIb19	Colorless, white	Oval	D = 6 L = 8	102.049 (30)B	Colorless with straight white stripes

Table 1. Continued.

Technique	Kidd code	Color	Shape	Dimensions (mm)	Reference number	Comments
Drawn	IVbb	Turquoise blue, red, white	Round	D = 7	5051 (1046)	Turquoise blue with red-on-white straight stripes; white is mixed lead-alkali glass
Drawn	IVbb	Black, red, white, dark blue	Round	D = 5 L = 5	3573 (5530)C	Red glass on a black core; dark blue-on-white straight stripes
Wound	WIb	Turquoise blue	Roundish	D = 7	33335 (19391)A	
Wound	WIb	Turquoise blue	Roundish	D = 7	33335 (19391)B	
Wound	WIb	Dark blue	Round	L = 12.5 Int. D = 4	48259 (19969)	Mixed alkali glass
Wound	WIb	Black	Roundish	D = 3-4	7401 (5580)	
Wound	WIb	Opalescent white	Roundish	L = 8	9421 (12217)	Potash glass
Wound	WId	Turquoise blue	Annular	D = 9	3187 (2333)	
Wound	WIIb	Tsp. purple	Tabular disk	D = 8 L = 3	10155 (10628)	
Wound	WIId	Colorless	Raspberry	D = 12 L = 8	44076 (22711)	Potash glass
?	?	Turquoise blue	Melon	D = 12 L = 6-7 Int. D = 6	10211(10960)	Faience?
Drawn	IVbb'	Red, white, dark blue	Round	D = 6	5080 (2710) core (C), dark blue (B), red (R)	Red-on-beige core; spiral dark blue-on-white stripes
Blown	BIa	Colorless	Round	D = 7	13420 (16859)	Sphere with very thin walls
Wound	WIIIb	Green, white	Round	D = 7	30024 (16.438)	White decoration is mixed lead-alkali glass
Wound?	WId?	Tsp. greenish	Annular	L = 4	106.001 (59)A	Bead fragment or vessel adornment
?	?	Colorless	Faceted	D = 12.5	13118 (6169)	
Drawn	If	Dark blue	Cornerless cube	L = 7	7576 (11598)	
Mold-Pressed	MP	Tsl. red	Faceted, drop-shaped	D = 8 L = 13	44076 (22709)	Mixed lead-alkali glass
Wound	WII	Black	Conical with 6 knobs around the middle	D = 12 L = 5	3208 (4684)	
Drawn?	?	Dark blue	Grain-shaped	D = 6-7.5	5113 (1389)B	

Reference numbers with a 10X.0XX(XX) format designate the Jardins du Carrousel site. Other reference numbers designate the Cours Napoléon site. Compositions are indicated in the Comments column for those samples that are not made of soda-lime glass.

Table 2. Paris Glass Samples Analyzed Using LA-ICP-MS.

Technique	Kidd code	Color	Shape	Dimensions (mm)	Reference number	Comments
n/a	n/a	Black	n/a	L = 45	24075 (10.1999)	Ceramic fragment with glaze on one side and a thick and irregular (1-5 mm) layer of glass on the other
Drawn	Ia?	Black	Round x-section	D = 4-6 L = 33	13.314 (15160)	Tube sealed at one end; mixed alkali glass
n/a	n/a	Dark blue	Square x-section	D = 4-5	5076 (1197)	Square and flaring tube with blobs of glass applied to the larger end
Drawn	Ia	Dark blue	Round x-section	D = 10 L = 29 T = 2.5	51.115 (19658)	Tube
Drawn	Ia	Greenish	Roundish x-section	D = 10 L = 12.5 T = 4	106.005 (47)A	Tube
Drawn	Ia	Turquoise blue	Roundish x-section	D = 6 L = 9 T = 2	106.005 (47)B	Tube
Drawn	Ia	Dark blue	Round x-section	L = 11	106.035 (22)B	Tube
Drawn	Ia	Dark blue	Round x-section	D = 8 L = 13 T = 2	106.036 (62)A	Tube
Drawn	Ia	Tsl. brown	Round x-section	D = 12 L = 10 T = 2	106.036 (62)B	Tube
n/a	n/a	Tsl. greenish	n/a	30 x 15	15445 (18196)	Raw glass attached to refractory material; lead glass
n/a	n/a	Tsl. greenish	n/a	L = 18	24019 (12278)	Waster containing unmelted quartz/mineral grains; potash glass
n/a	n/a	Tsl. greenish	n/a	D = 18	9596 (15.273)	Waster
n/a	n/a	Black	n/a	25 x 2	3168 (12471)	Waster; high lime glass

Reference numbers with a 10X.0XX(XX) format designate the Jardins du Carrousel site. Other reference numbers designate the Cours Napoléon site. Compositions are indicated in the Comments column for those samples that are not made of soda-lime glass.

Concentrations for major elements, including silica, were calculated assuming that the sum of their concentrations in weight percent in the glass is equal to 100% (Gratuze 1999).

Fully quantitative analyses are possible by using external standards. To prevent matrix effects, the composition of standards has to be as close as possible to that of the samples. Three different types of standards are used to measure major, minor, and trace elements. A standard reference material (SRM) is NIST SRM 610, a soda-lime-silica glass doped with trace elements in the range of 500 ppm. Certified values are available for a very limited number of elements. Concentrations from Pearce et al. (1997) were used for the other elements. Corning Glasses B, C, and D match compositions of ancient glass (Brill 1999, 2:544). An in-house standard with composition determined by Fast Neutron Activation Analysis was also used.

The detection limits range from 0.1 to 0.01% for major elements and from 20 to 500 ppb for others. Accuracy ranges from 5 to 15% depending on the elements and their concentrations. A more detailed account of the performances of this technique can be found in Gratuze (1999).

THE RESULTS

The summarized compositions of the artifacts from the Cours Napoléon and the Jardins du Carrousel sites, including maximum and minimum concentrations for the major and minor elements for the groups described below, are provided in Table 3. For polychrome glass beads, the different colors were analyzed separately. In some cases, however, the composition of some colors was not determined as it did not seem possible to sample only one color without contamination from adjacent ones. While most of the glass samples had a soda-lime composition, the glass samples that had a different composition will be described first.

Lead Glass

Four samples have lead oxide as the principal constituent in the glass (PbO > 50%). For three of them, the lead oxide concentration is close to 73%. Two of the beads are emerald green (samples 28551 [17169] and 106.001 [59]A) and one is transparent yellow (6066 [2857]). In these beads, the concentration of all the constituents, excepting lead oxide and silica, is less than 1%. The green color is due to the presence of small quantities of copper in the glass. No coloring element was intentionally added to the yellowish glass; quite likely the presence of iron and the absence of a decolorizer produced this color.

The fourth lead-glass artifact, sample 15445 (18196), is a small chunk of greenish glass that contains 55% lead oxide, 40% silica, and 3% potash. This sample also has notably low values of iron oxide and alumina suggesting that a very pure source of silica was used. Its color is probably due to the presence of small quantities of copper oxide (0.2%). The lead-glass beads and this small chunk are quite likely not related as their composition differs significantly.

Lead glass was present in Europe during the medieval period (Wedepohl et al. 1995) with a composition extremely similar to that of the lead-glass beads found at the Louvre sites. A lead-glass bead was identified in Rouen at a site dating from the 17th century (Dussubieux 2009). The three high-lead glass beads from the Louvre confirm that lead glass was used in Europe for the production of glass beads during the post-medieval period.

Mixed Lead-Alkali Glass

Two samples have a mixed lead-alkali composition: a lead-potash, gold ruby glass (44076 [22709]) and a lead-soda-lime emerald glass (30024 [16.438]). Sample 44076 (22709) contains 13% potash, 19% lead oxide, and almost 4% lime and soda. Other constituents in significant quantities are arsenic oxide (1.5%) and antimony oxide (2%). This artifact also contains 83 ppm of gold, 0.1% tin oxide, and 0.5% chlorine. Its composition is extremely similar to that of some 18th- to 19th-century beads presumed to be made in Venice and found at a site located in Washington state

Table 3. Minimum and Maximum Concentrations for Each Glass Group (in weight percent or ppm of oxides).

	Lead glass		Mixed-lead-alkali glass		Potash glass		Mixed alkali glass		Soda-lime glass	
Na_2O	0.02%	0.9%	3.6%	10.1%	0.2%	1.9%	6.1%	7.3%	8.2%	19%
MgO	117	204	0.6%	2.3%	0.4%	0.8%	0.8%	2.5%	0.7%	4.0%
Al_2O_3	0.1%	0.4%	1.0%	1.6%	0.2%	4.4%	2.1%	2.1%	0.5%	4.3%
SiO_2	24%	39%	50%	57%	60%	74%	59%	75%	57%	76%
K_2O	0.05%	3.3%	1.5%	13%	13%	20%	7.4%	8.5%	0.6%	7.0%
CaO	0.28%	0.65%	3.9%	7.9%	4.9%	12%	2.4%	10%	3.3%	16%
Fe_2O_3	0.05%	0.12%	0.6%	1.6%	0.3%	636	0.8%	1.5%	0.3%	3.6%
PbO	55%	73%	6.6%	19%	26	801	0.4%	111	0.1%	855

(Burgess and Dussubieux 2008). By comparison with those beads, this bead may belong to the late 18th century.

Ancient recipes report two main processes for achieving gold ruby glass. The first one, known as purple of Cassius, involves the precipitation of gold in a tin chloride solution. It was widely used in northern Europe starting in the last quarter of the 17th century. The second process involves the use of an arsenic compound along with gold. It is described in Venetian recipes dating from the end of the 17th century but was probably discovered in France by Bernard Perrot during the same period. The analysis of the French and Venetian lead-potash ruby glasses reveals the absence of tin and a low level of chlorine (Biron et al. 2011).

Bead 44076 (22709) contains chemical traces of both recipes but with respect to soda, the chlorine value for this glass is too high to have been caused only by the fluxing agent. Moreover, the tin concentration is more in agreement with that found in ruby glasses made using the purple of Cassius recipe. It is thus highly probable that arsenic was added to the glass batch as a refining agent. The use of both antimony and arsenic to eliminate bubbles in glass was already known by the end of the 17th century (Moretti 2002:122)

Sample 30024 (16.438) is a decorated emerald-green bead colored using copper. It contains 15.6% lead, 9.8% soda, 7.4% lime, and 5.9% potash. This composition may also be related to Venetian production.

The white glasses used to decorate beads are also part of the mixed alkali-lead glass group. Included are a turquoise blue, barrel-shaped bead with three red-on-white stripes (5051 [1046]), a dark blue, olive-shaped bead with four blue-on-white spiral stripes (2068 [1261]), and a colorless spherical bead with white stripes (17498 [18032]). Lead in the white glass is part of an opacifying agent that contains approximately 55% tin oxide and 45% lead oxide. The reduced composition of the different white glasses is approximately 66% silica, 13% soda, 10% lime, 3% potash and magnesia, and 1.5% alumina. The other colored glasses of these beads have the same reduced composition; they are made from a typical soda-lime glass that will be discussed below.

Potash Glass

Four samples have a composition where potash is more abundant than soda. Three beads (44076 [22711], 9421 [12217], 13118 [6169]) have potash-lime compositions. Beads 44076 (22711) and 13118 (6169) are composed of a colorless glass. Bead 44076 (22711) contains 13.5% potash and 9% lime. Arsenic oxide is the only other constituent (aside from silica) that is present with a concentration higher than 1%. Arsenic could act both as a decolorizer and a refining agent. Bead 13118 (6169) has a similar composition for major elements even if the concentrations of potash and lime are slightly higher (20% and 10%, respectively). To obtain a colorless aspect, no significant amount of arsenic was added to the glass but a very pure sand with very low concentrations of iron was used instead. The presence of manganese oxide (0.18%), which acts as a decolorizer, was also noted.

Bead 9421 (12217) is opalescent white with slightly more potash (18.6%) and slightly more lime (12%) than the previous bead. It contains more than 5% phosphorus. The presence of this element in a relatively high concentration suggests that this glass may have been opacified by introducing bone ash into the glass batch.

The last potash-rich sample (24019 [12278]) is identified as a waster. Its composition differs from that of the beads by having a higher alumina concentration (~ 4.5% instead of a maximum of 1.8%). Trace elements are also significantly different in this sample, indicating that this glass was not used in the production of the potash beads.

Potash glass dating from the 17th to 18th centuries is generally associated with a Bohemian origin.

Mixed Alkali Glass

Two glass artifacts (bead 48259 [19969] and tube 13.314 [15160]) exhibit similar quantities of soda (7% and 6%) and potash (7.5% and 8.5%). The tube has higher magnesia and lime concentrations compared to the bead (10% instead of 2% and 2.5% instead of 0.8%). It is colored with cobalt (> 3000 ppm) and contains a wide range of elements that may have been added to the glass along with the cobalt colorant: copper, arsenic, bismuth, uranium, and lead. These elements characterize the Erzgebirg cobalt mines exploited during the 16th and 17th centuries in Europe (Gratuze et al. 1996).

Bead 48259 (19969) is colored with copper (copper oxide concentration is 3.4%). Surprisingly enough, the composition of this bead, including major, minor, and trace elements, is identical to that of the beads produced during the final Bronze Age at the site of Frattesina and at other sites located in the northern part of Italy (Biaviati and Verità 1989; Brill 1992). Not only the composition but also the typology of the bead matches that of material associated with the Bronze Age. In France, a similar bead was found at Fort Harrouard, a late Bronze Age site located to the south-west of Paris (Gratuze et al. 1998). It is therefore possible that the bead is from the Bronze Age but was reused in the 17th or 18th century.

High-Lime Glass

Sample 3168 (12471), a glass waster, has an extremely high lime concentration (26%) together with a low alkali content (Na_2O = 0.4% and K_2O = 2%) and an unusually high alumina concentration (7%). This object also contains high amounts of the following oxides: iron (2.8%), copper (5.2%), and zinc (3.2%). Aside from the presence of copper and zinc, this composition appears to be very close to that of early 19th-century glass bottles such as the ones discussed by Berthier (1834). The only particularity of this glass seems to be the presence of copper and zinc, which is not mentioned in old texts. This sample is probably not related to glass beadmaking.

Unusual Compositions (Non Glass)

Three objects have compositions that do not correspond to glass and appear to be faience. Samples 5113 (1347) and 22.055 (11852) are black beads that have a thin vitrified outer layer and a core of an extremely heterogeneous and non-vitrified material as observed on broken beads. Their structure is closer to that of faience. Both beads share very low concentrations of soda, potash, and magnesia and relatively high concentrations of alumina (> 5%) and phosphorus oxide (3% and 5%, respectively). The coloring agents are different for the two specimens. Bead 5113 (1347) contains high concentrations of manganese oxide (14-20%), iron oxide (4%), and cobalt oxide (2700 ppm). Abnormally high concentrations of the following oxides were also measured: zinc (1.2%), arsenic (0.27%), bismuth (0.57%), and nickel (0.07%). If it is difficult to explain the presence of so much zinc, it seems quite likely that the other elements were added unintentionally at the same time as the cobalt. Bead 22.055 (11852) contains 3.4% manganese oxide, 8% iron oxide, and 2% copper oxide. Cobalt oxide concentrations are much lower in this bead (~ 200 ppm). The compositions of these beads are unusual and they are not considered to be glass.

The third object (10211 [10960]) is an indented, annular blue bead containing 83% silica, 7% soda, and about 2% of lime, potash, and alumina. The coloring agent is copper oxide (1.5%) which may have been added as bronze waste (presence of 0.2% tin). This object is also likely faience and not glass.

Soda-Lime Glass

Most of the glass samples have a soda-lime composition (Table 4). Figure 1 shows the concentrations of soda, lime, potash, and magnesia for the samples in the soda-lime glass group. Despite the wide variation that appears in the concentrations of these constituents, no discreet groups were identified that could suggest the existence of different production sites or periods. The glasses will be discussed by color.

Table 4. Average Reduced Composition for the Soda-Lime Glass Samples.

	Average +/- standard deviation
Na_2O	13.4 +/- 2.4%
MgO	2.2 +/- 0.9%
Al_2O_3	1.6 +/- 0.7%
SiO_2	69.1 +/- 3.3%
K_2O	4.3 +/- 1.7%
CaO	8.2 +/- 2.0%
Fe_2O_3	1.2 +/- 0.8%

Opaque Red Glass

Two red glass samples were analyzed. Sample 5051 (1046)R comes from the red stripes on a turquoise-blue bead decorated with red-on-white stripes. Sample 5080 (2710)R is from the red layer of glass covering a beige core. Opaque red glass is generally sparsely used. Both samples are plant-ash soda-lime glass. Different plants may have been used, however, as different concentrations of magnesia and potash were measured. Sample 5051 (1046)R contains 3.5% magnesia and 2% potash whereas sample 5080 (2710)R contains less magnesia (2.2%) but more potash (5%). Coloring recipes, which involve the use of copper, also differ. Sample 5080 (2710)R contains 1.7% copper oxide along with 3.6% tin oxide and 3.6% lead oxide. In sample 5051 (1046)R, a smaller quantity of copper was added to the glass batch (0.9%). Significant quantities of lead and tin oxides were detected in this glass but the concentrations for these two constituents are much lower than for 5080 (2710)R (0.3% and 0.2%, respectively). In both samples, iron oxide is present in rather high concentrations. They contain more than 3% whereas the average concentration for this constituent in all the soda-lime glass is 1.2%. Iron may have been used to facilitate the growth of metallic copper crystals in the glass as this element can act as an internal reducer.

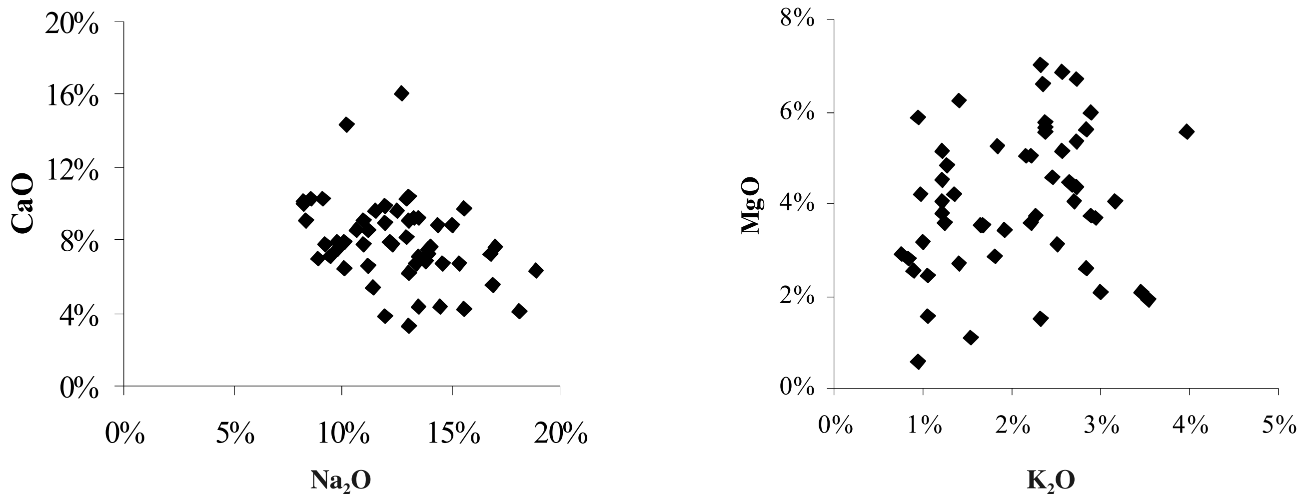

Figure 1. Two biplots (Na_2O-CaO and K_2O-MgO) for the soda-lime glass samples.

Manganese-Black and Cobalt Dark-Blue Glasses

"Black" glass is quite often not really black but blue, green, brown, or purple, and it is the saturation of the pigment in the glass that makes it look opaque and black. Soda-lime glass that is either dark purple (due to manganese) or dark blue (due to cobalt) is discussed here.

While sample 10155 (10628) only contains 1.8% manganese oxide and appears purple, eight beads contain high amounts of this constituent with concentrations ranging from 4% to 11% and appear black (12413 [7587], 3208 [4684], 7401 [5580], 5076 [1197], 106.035 [22]A, 9083 [3654], 5113 [1387], and 3218 [4349]). The composition of these beads is quite uniform: soda ranges from 8% to 13%, potash from 3.7% to 6.7%, lime from 7% to 10%, and magnesia from 2.4% to 2.8%. Iron oxide concentrations vary from 0.6% to 2%. Some samples also contain small amounts of the following oxides: copper (up to 0.4%), tin (up to 1.3%), arsenic (up to 0.5%), and lead (up to 1%). Two of these beads contain large amounts of cobalt (0.32% and 0.16%, respectively).

Ten dark blue glass beads contain cobalt oxide values ranging from 0.07% to 0.3%. All these samples contain much lower concentrations of manganese oxide than the manganese beads; from 0.05% to 2.1% with an average value of 0.68% (Figure 2).

High quantities of arsenic, nickel, and bismuth were detected in all the beads. These elements were quite certainly added unintentionally to the glass batch with the cobalt colorant (*see* the mixed alkali-glass section [p. 32] for more details).

Copper Turquoise-Blue Glass

Sixteen samples are of turquoise-blue glass colored with the use of copper with concentrations ranging from 0.8% to 2.7%. The presence of elements such as lead, tin, and zinc in some turquoise-blue glass reveals that the copper was introduced to the glass batch as brass or bronze. Most of the turquoise-blue glass samples have magnesia concentrations that are lower than the ones in the other glasses whereas the concentration of potash is in the same range compared to the other glass samples (Figure 3). It is interesting to note that sample 7576 (11598), a cornerless-cube bead, is dark blue although it does not contain cobalt but copper (2%).

Colorless Glass

Five colorless glass samples were analyzed: 17498 (18032)B, 13420 (16859), 102.049(30)B, 106.001(59)C, and 26037 (15067). These contain low concentrations of

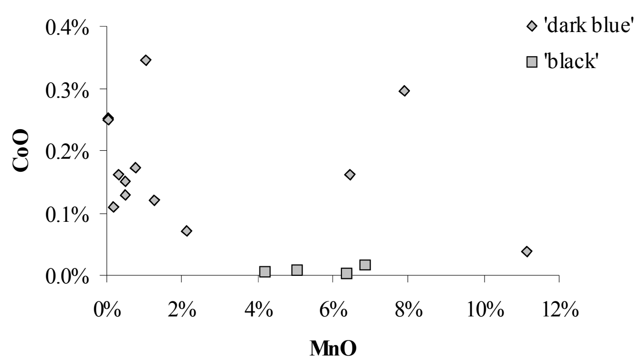

Figure 2. Biplot MnO-CoO for the "dark" glass samples.

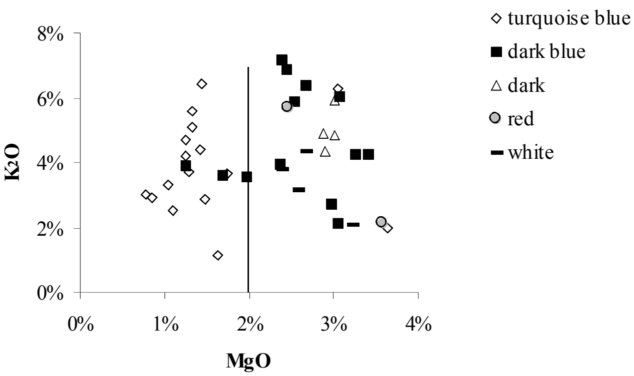

Figure 3. Bi-plot MgO-K_2O for the soda-lime glass.

iron oxide (with the exception of 13420 [16859]) and small amounts of manganese oxide (0.3-0.6%). The exception differs from the other three. Indeed, in addition to a higher iron oxide concentration, this sample has a high lime concentration (16%) which is much higher than that in the other colorless samples. This bead is a small glass sphere. It looks like a 17th-century imitation pearl. These were made of glass coated on the inside with a substance derived from fish scales called *essence d'Orient* (Riols 2011). These beads were marketed as "Parisian pearls or French pearls."

Greenish and Amber Glasses

Greenish (106.005 [47]A, 9595 [15.723]) and amber (33335 [19404], 106.036 [62]B) glass samples have concentrations of iron and manganese oxides that vary from 0.5% to 1.0% and 0.03% to 1.0%, respectively. Careful control of the atmosphere in the furnace may have been used to achieve the different colors.

DISCUSSION

The majority of the beads from the Jardins du Carrousel are of the soda-lime type whereas a larger range of compositions was identified for the material from the Cours Napoléon. This observation reflects the greater diversity in terms of the types of material recovered from the Cours Napoléon. Soda-lime glass was used for the earliest material which consists of drawn beads and tubes. If the use of soda-lime glass continued later on, new compositions may have been introduced later in the 17th century and during the 18th century to accommodate a larger range of colors and degrees of transparency. More diversity in manufacturing techniques appears during this period as well.

Karklins (1983) associates potash glass with the production of wound beads and soda-lime glass with drawn-bead technology during the 17th and 18th centuries. At the two Parisian sites, drawn beads are primarily made of soda-lime glass, whereas wound beads were manufactured from a variety of glass types. This may suggest a later date (late 18th to early19th centuries) for the wound non-potash beads. Archaeological evidence and the chemical composition of the beads suggest that as the demand for beads grew after the 16th century, their diversity increased as well.

Regarding the soda-lime glass, as elemental analyses of European post-medieval glass ornaments are unfortunately scarce, comparison of the compositional data from the Louvre sites is limited to two sites in The Netherlands (Karklins et al. 2001, 2002) and one in Rouen, France (Dussubieux 2009), all dating to the 17th century. (Soda-lime glass was manufactured in Venice, but analytical data from this major beadmaking center is non-existent.) These three sites primarily yielded soda-lime glass samples that were segregated into three different groups (Table 5) according to their lime, soda, and potash concentrations (Dussubieux 2009). While some of the Parisian soda-lime samples fall into these groups, a large proportion of them do not (Figure 4). Neither site can be associated more specifically with any of the three groups, but looking into glass coloring techniques does offer more opportunity for comparison.

An opaque red color is difficult to achieve and there were several recipes. For copper-red glass, it is necessary to add an internal reducer and to use a reducing atmosphere. One copper-red glass from the Louvre (5080 [2710]R) containing 3.6% tin and lead oxides is extremely similar to the copper-red glass from The Netherlands. In contrast, the composition of sample 5051 (1046)R does not match any of the Dutch or French compositions suggesting two other sources for the red glasses found at the Cours Napoléon.

White glass from the Cours Napoléon is made from a mixed lead-alkali glass containing tin. The use of tin as an opacifier in white glass seems related to earlier glass bead production from the 16th century to the very beginning of the 17th century (Karklins et al. 2001; Sempowski et al.

Table 5. Average Values for Na_2O, CaO, and K_2O for the Three Different Groups of Na-Ca Glasses Identified in The Netherlands and France (Dussubieux 2009).

	% Na_2O	% CaO	% K_2O
Group 1	17.4 +/- 1.0	5.9 +/- 0.8	2.5 +/- 0.7
Group 2	12.8 +/- 0.8	10.1 +/- 0.5	2.2 +/- 0.2
Group 3	12.0 +/- 1.9	8.2 +/- 1.5	4.5 +/- 1.2

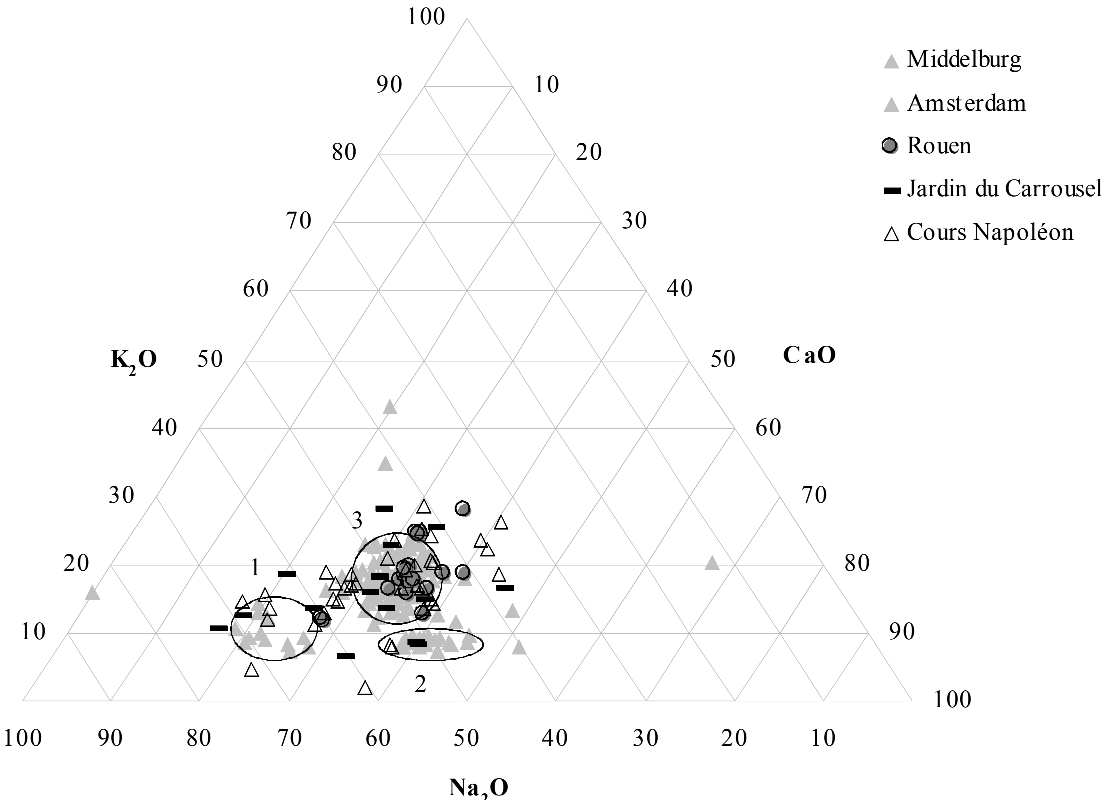

Figure 4. Na_2O-CaO-K_2O graph comparing soda-lime glasses from France (Dussubieux 2009) and The Netherlands (Karklins et al. 2001, 2002) and the soda-lime glass from Paris.

2000). White glass beads from Amsterdam and Middelburg do contain tin but in quantities lower (< 8.1%) than in the white Louvre glass. The white glass from Rouen has a very unique composition involving the presence of high quantities of tin (34%).

Turquoise-blue glass is always colored with copper with concentrations ranging from approximately 0.5% to 1.6%. Elements associated with copper (such as zinc, tin, and lead) exhibit different patterns but in general the proportion of tin and/or lead is more important in the turquoise-blue glass from the Louvre compared to the glass of the same color found in Rouen. No comparison was possible with the turquoise glass from The Netherlands as the concentrations of lead were not measured and tin has fairly high limits of detection (~ 1000 ppm).

Colorless and dark blue beads have more uniform compositions. Small quantities of manganese were used as a decolorizer in France and in The Netherlands, and cobalt associated with at least arsenic was detected in all the dark blue beads.

If some beads were imported (the potash beads were quite likely manufactured in Bohemia), the hypothesis of local bead production from imported or local raw glass or imported or local semi-finished products is more difficult to test. Sample 13.314 (15160) is a tube from the Jardins du Carrousel with one sealed end. This tube may have been used to manufacture beads but no firm conclusion can be made from just one sample. Additional possible evidence of local production is provided by the presence of sample 13420 (16859) which is a high-lime-glass sphere that could have been used to manufacture “Parisian pearls or French pearls.”

CONCLUSION

This study reveals that glass beads available in France after the 16th century were more diverse in terms of variety but also in terms of composition and, therefore, provenance, suggesting more interest in this kind of adornment. That some of the beads were imported from Bohemia is indicated by the presence of potash glass. While soda-lime glass is the most common type, its provenance remains undetermined. Different coloring technologies were used to achieve certain colors (such as red and white), suggesting that soda-lime glasses were manufactured at different periods or locations.

While the data presented herein do not resolve the problem of the provenance of glass beads found at French sites, it does show that investigating coloring techniques as well as chemical compositions can be useful. It is also clear that more comparative data are necessary. Indeed, while similar studies were conducted on glass beads from manufacturing sites in The Netherlands, there is a definite lack of data for contemporary beads produced in Venice. Venice produced a variety of glass objects using different recipes and complex technologies but, at this point, very little is known about the chemistry of Venetian glass beads.

It is hoped that this research will inspire more investigation into European glass beads to refine what is known about their production and distribution during the post-medieval period.

ACKNOWLEDGMENTS

The authors would like to thank Guillaume Fonkenell, Department of Sculptures and History of the Louvre Research Centers, for his help accessing the material included in this study. We also would like to thank Sophie Boucetta who photographed the samples. Part of this research was funded by a Guido Award from the Bead Study Trust in 2008.

REFERENCES CITED

Barrelet, J.

1953 *La verrerie en France de l'époque gallo-romaine à nos jours*. Larousse, Paris.

Bellanger, J.

1988 *Verre d'usage et de prestige*. Amateur, Paris.

Berthier, P.

1834 Traité des essais par la voie sèche: ou, Des propriétés, de la composition et de l'essai des substances métalliques et des combustibles. *À l'usage des ingénieurs des mines, des exploitants et des directeurs d'usines*. Tome 1:460-466. Thomine, Paris.

Biaviati, A. and M. Verità

1989 The Glass from Frattesina, A Glassmaking Center in the Late Bronze Age. *Rivista della Staz. Sper. Vetro* 4: 295-299.

Biron, I., B. Gratuze, S. Pistre, and P. Lehuédé

2011 Etude en laboratoires d'objets en verre attribués à Bernard Perrot. Etude en laboratoires d'objets en verre attribués à Bernard Perrot. *25èmes rencontres de l'AFAV, Orléans (France), Bulletin de l'Association Française pour l'Archéologie du verre 2011*:19-25.

Brill, R.H.

1992 Chemical Analysis of Some Glasses from Frattesina. *Journal of Glass Studies* 34:11-22.

1999 *Chemical Analyses of Early Glasses*. 2 vols. The Corning Museum of Glass, New York.

Burgess, L. and L. Dussubieux

2008 Chemical Composition of Late 18th- and 19th-Century Glass Beads from Western North America: Clues to Sourcing Beads. *Beads: Journal of the Society of Bead Researchers* 19:58-73.

De Raedt, I., K. Janssens, J. Veeckman, L. Vincze, B. Vekemans, and T.E. Jeffries

2001 Trace Analysis for Distinguishing Between Venetian and Façon-de-Venise Glass Vessels of the 16th and 17th Century. *Journal of Analytical Atomic Spectrometry* 16:1012-1017.

Dussubieux, L.

2009 Chemical Investigation of Some 17th-Century French Glass Personal Ornaments. *Journal of Glass Studies* 51:95-110.

n.d. Typological Study of French Glass Beads Dated from 16th to 18th Century A.D. Manuscript in preparation.

Egan, G.

2007 A Handful of History. *The Guild of Arts Scholars, Dealers, and Collectors, Newsletter* 6:5. <http://www.artsscholars.org/download/guild-newsletter-winter-07.pdf> (accessed 10 March 2012)

Francis, P., Jr.

1988 The Glass Trade Beads of Europe: Their Manufacture, Their History, and Their Identification. *The World of Beads Monograph Series* 8. Lake Placid, NY.

Gratuze, B.

1999 Obsidian Characterization by Laser Ablation ICP-MS and its Application to Prehistoric Trade in the Mediterranean and the Near East: Sources and Distribution of Obsidian Within the Aegean and Anatolia. *Journal of Archaeological Science* 26:869-881.

Gratuze, B., C. Louboutin, and Y. Billaud

1998 Les perles protohistoriques en verre du musée des Antiquités nationales. *Antiquités nationales* 30:11-24.

Gratuze, B., I. Soulier, M. Blet, and L. Vallauri

1996 De l'origine du cobalt: du verre à la céramique. *Revue d'Archéométrie* 20:77-94.

Guerrero, S.

2010 Venetian Glass Beads and the Slave Trade from Liverpool, 1750-1800. *Beads: Journal of the Society of Bead Researchers* 22:52-70.

Karklins, K.

1983 Dutch Trade Beads in North America. In "Proceedings of the 1982 Glass Trade Bead Conference," edited by Charles F. Hayes III, pp. 111-126. *Rochester Museum and Science Center, Research Records* 16.

Karklins, K., R.G.V. Hancock, J. Baart, M.L. Sempowski, J.-F. Moreau, D. Barham, S. Aufreiter, and I.T. Kenyon

2002 Analysis of Glass Beads and Glass Recovered from an Early 17th-Century Glassmaking House in Amsterdam. In "Archaeological Chemistry: Materials, Methods and Meaning," edited by K.A. Jakes, pp. 110-127. *ACS Symposium Series* 831. American Chemical Society, Washington.

Karklins, K., J. Kottman, R.G.V. Hancock, M.L. Sempowski, A.W. Nohe, J.-F. Moreau, S. Aufreiter, and I.T. Kenyon

2001 On the Chemical Variability of Middelburg Glass Beads and Rods. In *Australian Connections and New Directions*, Proceedings of the 7th Australasian Archaeometry Conference, edited by M. Jones and P. Sheppard, pp. 187-195. Department of Anthropology, The University of Auckland, New Zealand.

Kidd, K.E.

1979 Glass Bead-Making from the Middle Ages to the Early 19th Century. Parks Canada, *History and Archaeology* 30.

Kidd, K.E. and M.A. Kidd

1983 A Classification System for Glass Beads for the Use of Field Archaeologists. In "Proceedings of the 1982 Glass Trade Bead Conference," edited by Charles F. Hayes III, pp. 219-256. *Rochester Museum and Science Center, Research Records* 16.

Moretti, C.

2002 *Glossario del vetro veneziano, dal trecento al novecento* (parte seconda). Marsilio, Venice.

Pearce, N.J.G., W.T. Perkins, J.A. Westgate, M.T. Gorton, S.E. Jackson, C.R. Neal, and S.P. Chenery

1997 A Compilation of New and Published Major and Trace Element Data for NIST SRM 610 and SRM 612 Glass Reference Materials. *Geostandards Newsletter* XXI:114-115.

Riols, A.

2011 Les dernières perleuses de Langeac (Haute-Loire) 19e-20e s. *25èmes rencontres de l'AFAV, Orléans (France), Bulletin de l'Association Française pour l'Archéologie du verre 2011*:115-118.

Sempowski, M.L., A.W. Nohe, J.-F. Moreau, I.T. Kenyon, K. Karklins, S. Aufreiter, and R.G.V. Hancock

2000 On the Transition from Tin-Rich to Antimony-Rich European White Soda-Glass Trade Beads for the Senecas of Northeastern North America. *Journal of Radioanalytical and Nuclear Chemistry* 244(3):559-566.

Šmit, Ž., K. Janssens, E. Bulska, B. Wagner, M. Kos, and I. Lazar

2005 Trace Element Fingerprinting of Façon-de-Venise Glass. *Nuclear Instruments and Methods in Physics Research* B 239:94-99.

Turgeon, L.

2004 Beads, Bodies and Regimes of Value: From France to North America, c. 1500 - c. 1650. In *The Archaeology of Contact in Settler Societies*, edited by Tim Murray, pp. 19-47. Cambridge University Press, Cambridge.

2001 French Beads in France and Northeastern North America During the Sixteenth Century. *Historical Archaeology* 35(4):58-82.

Van Ossel, P.

1998 Les jardins du Carrousel (Paris), de la campagne à la ville: la formation d'un espace urbain. *Documents d'archéologie française* 73:379. Editions de la maison des sciences de l'homme, Paris.

Wedepohl, K.H., I. Krueger, and G. Hartmann

1995 Medieval Lead Glass from Northwestern Europe. *Journal of Glass Studies* 37:65-82.

Laure Dussubieux
The Field Museum, Anthropology Dept.
1400 South Lake Shore Drive,
Chicago, Illinois 60605
E-mail: ldussubieux@fieldmuseum.org

Bernard Gratuze
Institut de Recherche sur les Archéomatériaux
UMR 5060 CNRS/Université d'Orléans
Centre Ernest-Babelon
3D rue de la Férollerie, 45071 Orléans cedex, France
E-mail: gratuze@cnrs-orleans.fr