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A NOTE ON THE NEUTRON ACTIVATION ANALYSIS OF 16th AND 17th-CENTURY BLUE GLASS TRADE BEADS FROM THE EASTERN GREAT LAKES

By the late 16th century, European-made glass trade beads were reaching the Native peoples of the eastern Great Lakes. From this time until the mid-17th century beads of blue glass were widely traded items, being about as common in regions dominated by the French trade (Ontario) as by the Dutch (New York).

Although there is a wide range of blues observed in the glass trade beads of this period, there are two modal hues. One is a turquoise blue (hue about 2.5PB to 7.5B in the Munsell notation) called "robin's egg blue" in the Kidds' 1970 typological system (bead varieties IIa40,41,42, depending on the particular bead form), with some specimens tending towards "cerulean blue" (IIa44), "brite copen blue" (IIa45) and "shadow blue" (IIa46,47). The second modal blue is a very dark, more purplish blue (about 7.5PB) which is called "brite navy" in the Kidds' system (varieties IIa55,56,57, depending on shape). This is the same blue that appears on the outer layer of "star" or "chevron" beads (IIIk3, IIIm1).

Although certain bead types can be used to identify particiular time horizons or even European-centered trading zones, the turquoise blue beads (IIa40)

have an extremely wide time-space distribution; that is, their presence on a site is not diagnostic. Yet, do these IIA40 beads in fact represent a homogeneous group or are there subtle differences through time or over space? More generally, why do there seem to be two basic colors of blue in these early historic trade beads? Furthermore, why is there a tendency for the turquoise blue glass beads on late 16th-century sites to be found in a highly disintegrated condition? To answer these questions, it seems that we must go "into" the beads, and look at their chemical composition. Other chemical analyses incorporating Great Lakes material have been reported by Karklins (1983) and Lewis (1979).

Consequently, 88 blue glass beads were selected for non-destructive neutron activation analysis using the SLOWPOKE Reactor Facility at the University of Toronto. Ten chemical elements were sought: cobalt (Co), tin (Sn), copper (Cu), sodium (Na), aluminum (Al), manganese (Mn), chlorine (Cl), calcium (Ca), arsenic (As) and potassium (K). In addition, silicon content was measured in a subset of the bead samples. It would have been advantageous to have included iron (Fe) but unfortunately that would have required a neutron irradiation 1000 times greater, which would have left most of the beads slightly radioactive for more than a year. As it was, beads could be handled only 1-2 weeks after analysis.

The rationale for this particular selection of elements was that all of them produced, on neutron activation, short-lived radioisotopes, which decayed with the emission of characteristic gamma-rays, easily quantifiable with a gamma-ray spectrometer. The diagnostic suitability of these elements is that Co, Cu, and Mn are elements used commonly in pre-industrial glass technology to produce blue and purple colorations, while Sn is an opacifier. Glass is a randomly modified network structure, with the network made from oxides such as SiO_2 (silica), but modified by oxides of Na, K, Ca and Fe. Usually Na and/or K are present in large amounts (5-15%), at which level they act as a flux to lower the melting temperature of the raw material mixture. Another essential element was Ca, the presence of which in moderate amounts improves the resistance of glass to chemical attack. A common constituent of certain cobalt-containing ores is As. Chlorine and aluminum, while only minor elements, are sometimes very useful in

characterizing ceramic/glass materials.

To provide a time/space "grid" in which to examine for patterned chemical variations, beads were selected from a number of late 16th- and 17th-century sites in both Ontario (Huron and Neutral) and New York state (Seneca). Late 16th-century (ca. A.D. 1580-1600) samples included beads from the Molson and Kleinburg sites in Ontario and the Adams site in New York. The 17th-century samples (ca. 1620-50) derived principally from the Train, Ossossane, and Burke sites in Ontario, and the Warren and Cornish sites in New York.

Colorants

The two basic "blues" can be clearly associated with two principal colorants, copper and cobalt. Copper, specifically copper in its Cu(II) state, yields a turquoise color (i.e., "robin's egg blue"); in fact, the mineral turquoise itself is a copper compound. In contrast, cobalt produces a dark blue glass ("brite navy"), and it was widely used in ceramic decoration; for example, on English "old blue" printed earthenwares of the early 19th century. In none of the beads was Mn the principal colorant, although in some specimens there is a significant amount of Mn present. Manganese imparts a violet tinge to glass, perhaps best known to historical archaeologists in solar-oxidized, late 19th-century medicine bottles.

Despite the various shades of blue identified by the Kidds in their bead typology, all the beads so far examined can be assigned to the two major color groups: those principally colored with copper and those with cobalt. As a colorant, cobalt is 20 times as powerful as copper and 10 times as powerful as manganese. In some beads the addition of only 300ppm (0.03%) cobalt is sufficient to produce the characteristic dark blue glass. In turquoise beads, copper content ranges from about 0.6 to 2.0%.

Most beads examined are made of translucent glass, although this translucency is masked in copper-colored beads by the presence of numerous air bubbles. Certain beads, however, are noticeably opaque (type IIa46/48?). On analysis, these opaque beads were found to have significant quantities of tin (5-7%), which in the absence of a colorant produces an opaque white glass. Since

variety IIa46/48 beads contain significant amounts of cobalt, this tin and cobalt mix yields "pastel" blues.

There are certain temporal differences in the amounts of colorants. Late 16th-century copper-colored beads normally contain from 1.0 to 1.6% copper, while the 17th-century examples mostly range between 0.7% and 1.1%. The earlier beads, with their higher copper content, tend to visibly differ from later beads, the earlier ones displaying a more "intense" blue. Furthermore, there is some evidence for spatial variation in the Mn content of the copper-colored beads. A sample of beads from the 17th-century Seneca sites of Warren and Cornish, while having copper levels similar to contemporaneous Ontario sites, tend to have a higher manganese content: 9 of 12 beads from the Seneca sites have greater than 700ppm of Mn, compared to 7 of 28 for Huron/Neutral sites. In the high Mn beads, the "normal" turquoise color may have a slight violet tinge.

Major Elements

All of the non-disintegrated blue beads have relatively high amounts of sodium (about 7-14%) and low amounts of potassium (under 5%), thus confirming Karklins' (1983) observation that most drawn beads are soda glass in contrast to wound beads which are usually potash glass. There are, however, differences in the sodium content between 16th- and 17th-century copper-colored beads. The Na levels for the late 16th-century copper-colored beads mostly range between 7 and 11% compared to 10-13% for the 17th-century ones. The cobalt-colored beads tend to have relatively low sodium (7 to 10%).

There are also differences in calcium levels. The cobalt-colored beads have relatively high Ca (4-8%), whereas most copper-colored beads range between 1 and 5%. Once again, there are temporal differences within the group of copper-colored beads: the 16th-century beads are very low in calcium (most between 1 and 2%), while 17th-century ones display slightly higher levels (2-5%).

One characteristic of the late 16th-century copper-colored beads is their tendency to be found in a disintegrated state, sometimes consisting of nothing but a blue or green powder with glass particles reduced to the size of sand grains.

Analyses of such disintegrated beads from the Kleinberg, Molson and Adams sites reveal that the glass has been largely stripped of its sodium content (under 4%). It is perhaps significant that the 16th-century turquoise-glass beads in general have low Ca, particularly the disintegrated ones (0.5-1.5%). This suggests that these beads had an insufficient amount of calcium to prevent them from being chemically attacked. In contrast, the cobalt-colored beads, with their high Ca content, are not normally found in this disintegrated state.

Minor Elements

Chlorine ranges from about 0.5 to 2.1%, copper-colored beads displaying greater quantities than the cobalt ones. The chlorine content is closely correlated with Na levels, suggesting that the chlorine was added to the glass as an impurity in the soda ash.

Aluminum ranges from 0.3 to 1.2%, but there is no patterned variation with either time, space, or major colorant type.

The amount of arsenic is closely related to cobalt content. Since arsenic is present in many cobalt ores (e.g., cobaltite and skutterudite), the ratio of As to Co may ultimately prove useful in determining the cobalt source or sources used in coloring the dark blue beads.

Conclusions

The 16th- and 17th-century blue glass beads studied here have two basic chemically produced hues: turquoise blue (copper) and dark blue (cobalt), although variation exists depending on the particular amounts of these colorants as well as the presence of such color modifiers as manganese and tin. In the turquoise beads there are chemical differences through time, although it is presently unknown whether this represents a general change in manufacturing process or a shift in the source of supply. Spatial differences in the manganese content of the 17th-century copper-colored beads suggest the possibility of discriminating French and Dutch trade items, although more analysis is required to confirm this.

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References

Karklins, K.

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

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

1970 A Classification System for Glass Beads for the Use of Field Archaeologists. Canadian Historic Sites: Occasional Papers in Archaeology and History 1: 45-89.

Lewis, T.L.

1979 Neutron Activation Analysis of Glass Trade Beads. Unpublished manuscript.

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