

ANALYSIS OF DETERIORATING 19TH-CENTURY BLUE GLASS BEADS

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INTRODUCTION

The chemical deterioration of glass is not an uncommon phenomenon in cultural heritage collections. Crizzling, the process whereby the alkali in a glass is hydrolyzed and leaches out of the glass, eventually attacking the silica, is the most common form of glass deterioration. This is a well-studied process that generally follows a known progression from initial hydrolysis of the glass exterior to full fragmentation of the glass object. A 19th-century beaded picture from New York, United States (Figure 1), was exhibiting glass deterioration: blue beads were fragmenting while the other colors appeared stable. Upon further visual examination, the blue beads did not have any of the indicators of the earlier stages of crizzling, only the final fragmentary stage. These observations challenged the assumption that the beads were crizzling, leading to an investigation of the beads to learn more about the glass and its deterioration.



Figure 1: Wooster Sisters, Beaded picture, 1835-1855 CE, cotton plain-weave textile, cotton thread, glass beads, H 82 cm × W 66.5 cm. Garman Art Conservation Department, Private Collection.

METHODS

FTIR-ATR: Infrared spectra were collected using a Nicolet 6700 FTIR spectrometer with a Smart iTR ATR accessory (both Thermo Scientific). The spectra are the average of 32 scans at 4 cm^{-1} spectral resolution.

SEM-EDX: Secondary electron images were obtained using a Tescan Vega3 XMU tungsten variable pressure SEM. X-ray data were processed with an Oxford Instruments 50 mm^2 X-Max Silicon Drift Detector and AZtecEnergy software.

XRF: Spectra were collected using a Bruker Artax 400 energy dispersive X-ray spectrometer system. The excitation source was a rhodium target X-ray tube with a 0.2 mm beryllium window. X-ray signals were detected using Peltier cooled Xflash silicon drift detector.

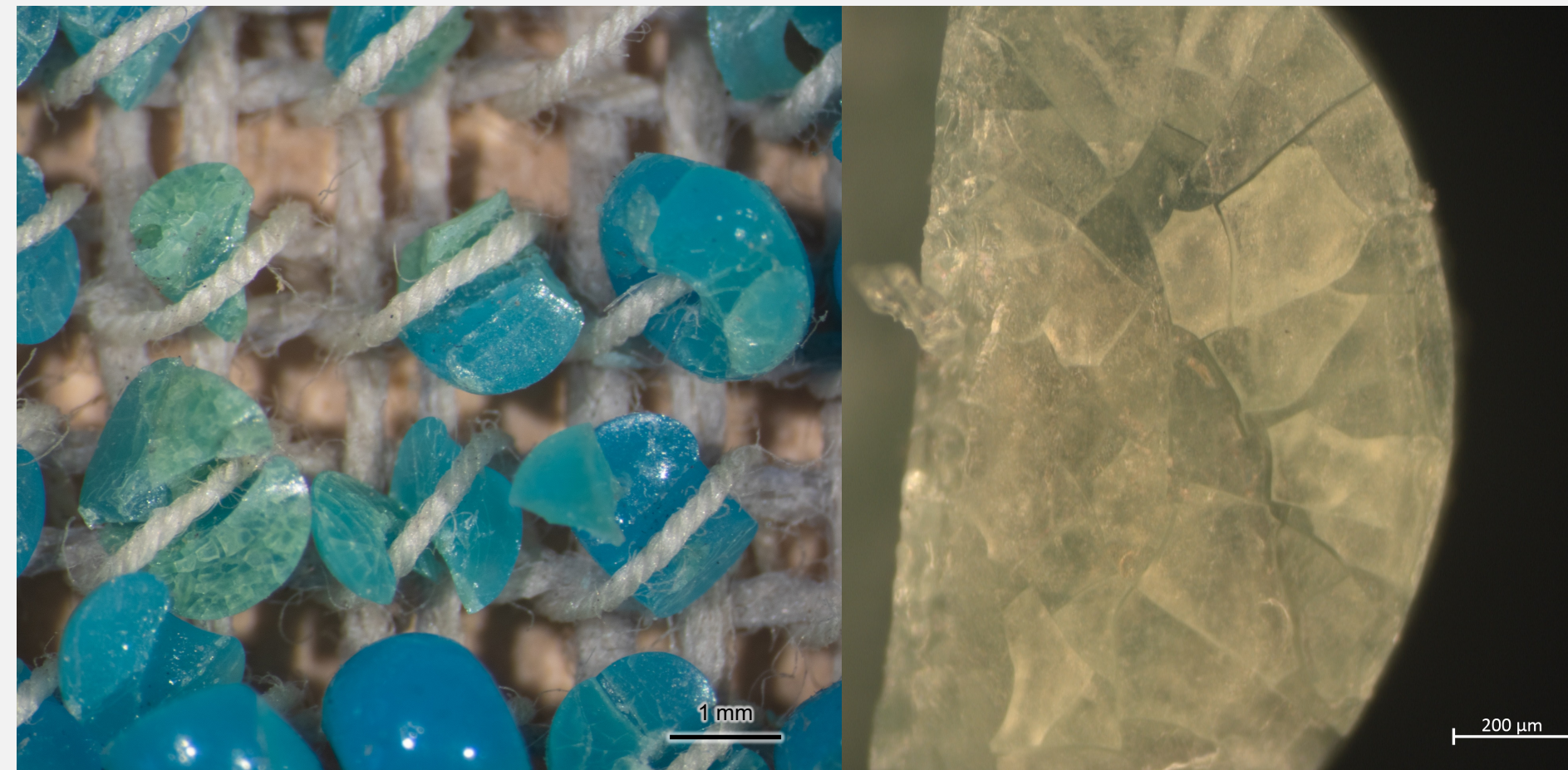


Figure 2: Photomicrograph of deteriorating beads

Figure 3: Photomicrograph of a sample bead

RESULTS & DISCUSSION

From initial visual inspection and observations using photomicrographs and microscopic techniques, it appeared that the beads were transitioning from stable to thoroughly cracked without passing through any intermediary stages of crizzling. Additionally, the most deteriorated bead fragments had changed color and opacity from a translucent bright blue to a milky muted green, with some also containing brown halos around cracks (Figure 2, 3). While changes in opacity are consistent with crizzling, neither the color change observed nor the brown halos around the cracks are. Bead fragments and intact beads were visually sorted into seven deterioration categories and analyzed with XRF, FTIR-ATR, Raman, and SEM-EDX.

Across all bead deterioration categories, copper and lead were the major elements detected by XRF. In the intact beads, potassium was also a major element. Calcium and iron were minor elements, and silicon and manganese were detected in trace amounts. This indicated a heavily leaded glass with copper as the primary colorant. FTIR-ATR and Raman spectroscopy results were less conclusive. FTIR-ATR spectroscopy on beads from the most-deteriorated and least-deteriorated categories showed a peak shift from 995 cm^{-1} in the least-deteriorated bead to 1015 cm^{-1} for the most deteriorated bead. This may indicate changes from bonds with lead cations to bonds with sodium ions (Moicciou et al. 2013, 134). Similar shifts were observed with Raman spectroscopy, and more deteriorated beads had significantly poorer signal than less deteriorated.

Finally, areas enriched in sodium (Figure 4) were detected using SEM-EDX. These areas may correspond to the hydrolysis of the alkali and were found along cracks and break edges in the bead fragments. To investigate if the alkali is leaching out onto the bead surface, a random sample of bead fragments across all deterioration categories were based and placed in the same mass of deionized water. The pH of the water was taken before and after the beads were added, and then after two hours. The pH of the water significantly increased with the addition of the beads, indicating that the bead fragments had free OH^- ions on their surfaces. These results indicated the beads were likely exhibiting crizzling behavior, the most common form of glass deterioration.

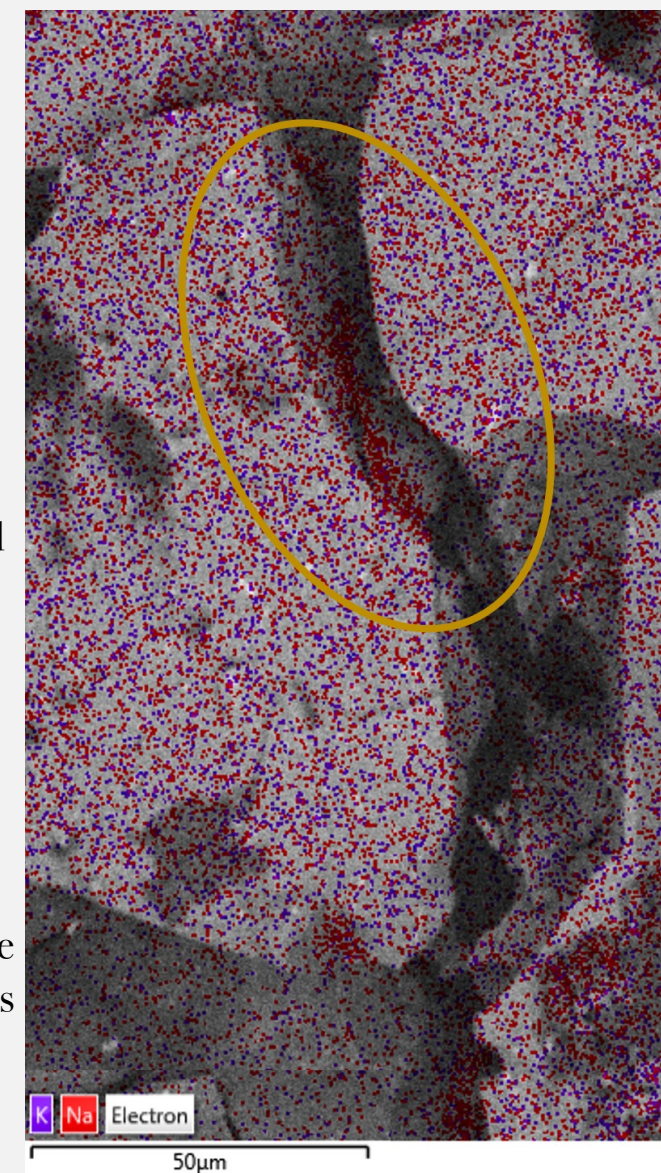


Figure 4: EDX map overlaying SEM image. The circled area is a crack edge that is enriched in sodium.

CONCLUSIONS

The deteriorating beads that were the subject of this study were made from a lead-potash glass colored with copper. It is likely that the beads are deteriorating primarily due to the hydrolysis of the alkali in the glass matrix, a phenomenon known as crizzling. However, the beads are not following the expected behavior of crizzling glass, leading to the potential for a second, undetected, method of deterioration such as additional depolymerization of the glass matrix. However, it is also possible that the unusual presentation of crizzling is due to the manufacture of the beads. These beads were likely quickly and inexpensively made for an export market, so an unbalanced glass batch or improper annealing could have created significant internal stress in the beads. When the bead began the initial stage of crizzling, this slightest change in surface could have been enough to react with the internal stress to fully fragment the bead. These hypotheses are untested and warrant further investigation.

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