Multi-technique approach to unveil the composition, fabrication, and potential provenance of a unique pre-Roman glass collection (IV-I BC)

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***Abstract* – This work summarizes the results of a three-year project focused on the archaeometrical study of a collection of about one thousand pre-Roman glass beads found at the archaeological site of Pintia (Valladolid, Spain), located at the interior of Iberia. In addition to the morphological and contextual analysis of the entire collection, a representative set of 150 samples, including several unique and exquisite polychrome beads, have been studied in detail by diverse archaeometric techniques such as Raman spectroscopy, X-ray fluorescence, PIXE/PIGE, X-ray tomography, among others. The combined use of these techniques provided valuable data about the production processes of the polychrome beads. Remarkably, some previous conceptions about their fabrication have been modified, and evidence about their production in secondary workshops has been provided. Moreover, hints about the origin of the primary glasses employed in all the studied samples have been obtained, suggesting their origin was scattered between Egypt and Syria-Palestine.**

I. INTRODUCTION

Although nowadays a common product, glass was considered a most valuable material during the Protohistory, widespread mainly by Phoenicians along the Mediterraneum from the primary production sites at Syria-Palestine and Egypt.[1–4] Although blue glass beads are the most common pre-Roman glass beads, exquisite polychrome pieces are not rare, reaching the summit of glass craftsmanship at that age with the production of the Phoenician glass pendants.[1,2]

A remarkable collection of about one thousand pre-Roman glass beads has been recovered at the necropolis of "Las Ruedas" at the archaeological site of Pintia (Padilla de Duero, Valladolid, Spain) (Figure 1), suggesting strong commercial and political relationships with other Iberian and Mediterranean cultures.[5]

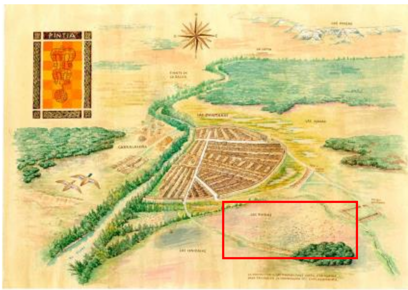


Fig. 1. Recreation of the vaccean settlement of Pintia. The location of the necropolis of "Las Ruedas" is indicated with a red rectangle.

Herein, the first complete and comprehensive archaeometric analysis of this extraordinary collection is presented. The complementary use of X-ray tomography, X-ray fluorescence, Raman spectroscopy, and PIXE/PIGE have revealed hidden details about their manufacturing process, the pigments employed in each glass phase, and providing evidence about the existance of a secondary workshops and the provenance of the primary glasses.

II. MATERIALS AND METHODS

A. Samples

A representative selection of about 150 pieces from the collection of glass beads recovered at Pintia have been choosen for this work (Figure 2). This selection included all the polychrome glass beads recovered (Figure 3), as well all the pieces recovered from closed contexts (i.e., burials). It should be noticed that a few of these burials provided a significant number of beads, probably composing a collar (Figures 4.a and 4.b), while in others only a few beads have been found (Figure 4.c).

Fig. 2. Prof. Dr. Carlos Sanz-Minguez (CEVFW, AHMAT) classifying the pre-Roman glass beads collection studied in this work.

Fig. 3. Pictures of some of the polychrome pre-Roman glass beads studied.

a) *b)* *c)*

Fig. 4. (a) Objects recovered at burial 247b, (b) where a large number of glass beads were recovered. (c) Objects recovered at burial 128, where a couple of green glass beads were found.

B. Experimental Techniques

X-ray tomography of the glass beads was performed using a GE PHOENIX V|TOME|X S 240 at the Microscopy and Microcomputed Tomography laboratory at CENIEH facilities with the collaboration of CENIEH Staff.

The elemental composition of the glass beads was studied, on the one hand, by using the M4 TORNADO Energy Dispersive X-ray fluorescence spectrometer (Bruker Nano GmbH, Berlin, Germany). This instrument is equipped with a micro-focus side window Rh X-ray tube powered by a low-power HV generator and cooled by air. On the other hand, PIXE (particle induced X-ray emission) and PIGE (proton induced gamma-ray emission) measurements were carried out at NewAGLAE facility (C2RMF, Paris, France) (via IPERION HS, EU Transnational Access programme). Multivariate statistical analysis performed in R was used in the analysis of the data. The results were displayed using principal component analysis (PCA) with preference for those principal components (PC) describing the most variation.

Finally, a high-resolution Horiba-Jobin Yvon LABRAM HR 800 UV Raman spectrometer, with solid-state laser (532.8 nm), an Olympus BX41 microscope, and a Symphony CCD detector, was employed to study the glass beads by Raman spectroscopy in microscopic backscattering mode with 100x magnification.

III. RESULTS AND DISCUSSION

The study by X-ray tomography of pre-Roman polychrome glass beads have evidenced its potential to differentiate the diverse glass phases. In particular, it is possible to identify phases with diverse X-ray absorbance, related to the use of pigments including heavy elements (e.g., Sb, Pb). Accordingly, yellow phases present higher X-ray absorbance than white phases, and those higher than yellow/green phases (Figure 5). Moreover, cross-sections of the 3D tomographic reconstructions evidence the presence of air bubbles inside the glass, which shape and presence sometimes provide information about their production process (Figure 5).[6]

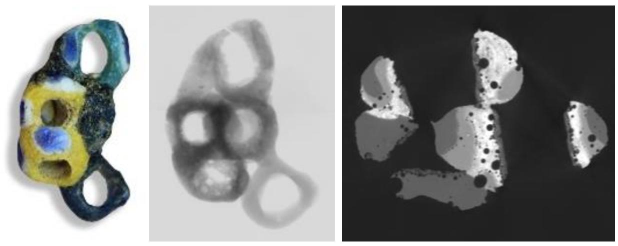


Fig. 5. Picture of a polychrome glass bead (left), corresponding projection (i.e., X-ray radiograph) obtained at this orientation (center), and cross-section of the 3D tomographic reconstruction showing the diverse glass phases of several individual beads (right).

Then, the elemental composition mapping achieved by X-ray fluorescence provided hints about which differential elements, generally chromophores, are present on each of these phase (Figure 6). As an example, blue glass phases are generally characterized by the presence of Co, Mn, and/or Cu, green phases present Cu, white phases present Ca, Sb, and/or Ti, and yellow phases present Pb and sometimes Sb and Sn (Figure 5). Moreover, a deeper study of these glass phases at microscopic level combining X-ray fluorescence and Raman spectroscopy allows a precise identification of the pigments employed to achieve the diverse colors. As an example, yellow phases are generally related to the presend of Pb oxides and Naples yellow (Figure 7).[7,8] A relevant result obtained in this work is the presence of glass phases with the same color but different composition, in terms of the employed pigments, in the same polychrome bead. This unexpected result suggests the production of such pieces in secondary workshops from primary glass ingots (i.e., the crafsman produced the pieces from colored glass, regardless of their provenance and composition).

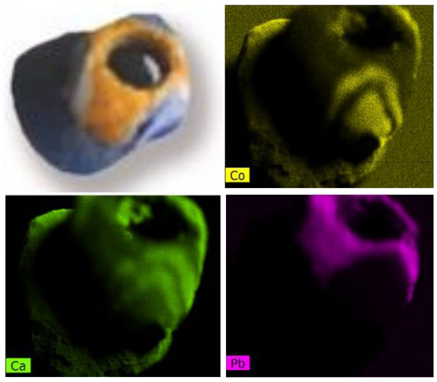


Fig. 6. Picture and X-ray fluorescence elemental compositional maps of a polychrome bead, showing the distribution of Co in the blue phase, Ca in the white phase, and Pb in the orange phase.

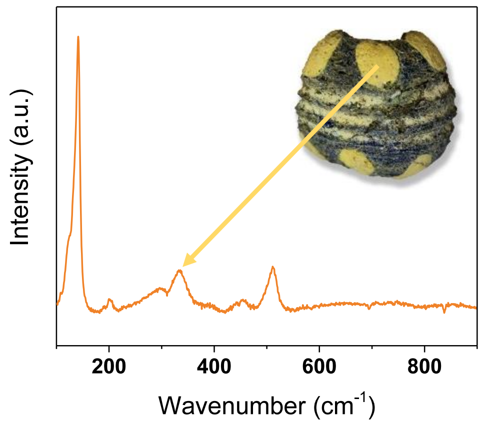
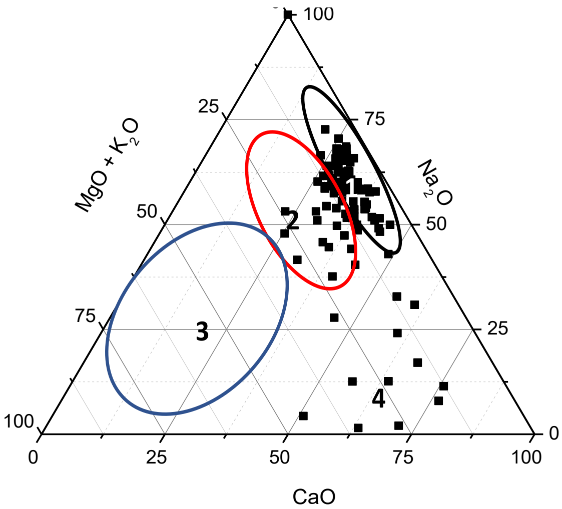


Fig. 7. Representative Raman spectra of the yellow phase (lead oxides and Naples yellow) of a polychrome bead.

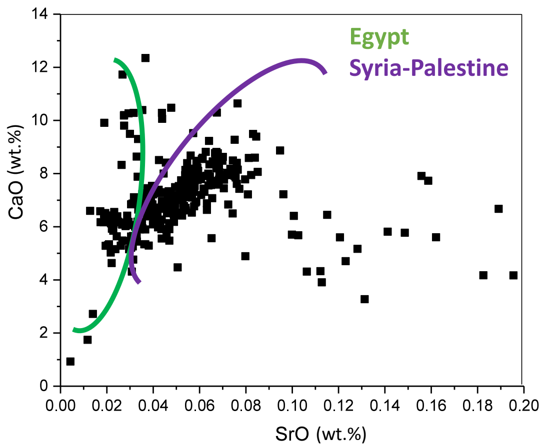
Finally, the study of the composition of the glass phases was completed by more accurate techniques such as PIXE/PIGE, which in the case of PIGE can also provide information about the inner unaltered glass. On the contrary, X-ray fluorescence data are usually affected by surface alterations.

PIXE/PIGE results allowed classifying the large set of samples studied by the composition of the glass matrix, showing the existance of two main groups of samples: natron soda-lime and plant-ashes soda-lime glass (Figure 8.a).[3] Moreover, some samples present compositions compatible to a third group, which has been generally retated to forest plant-ashes potash-lime glass. However, as this composition is not generally expected at that age, further analysis should be performed on these samples.

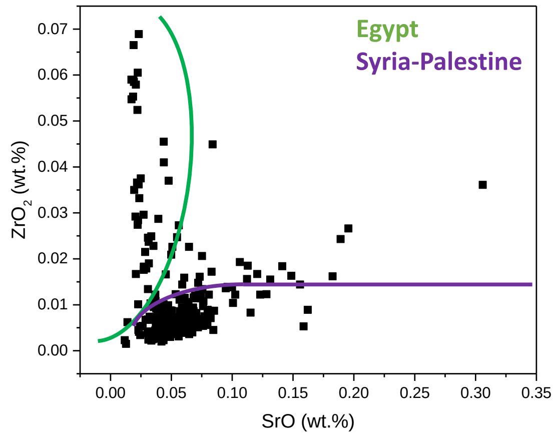
In addition, the ratios between some oxides, such as CaO and SrO, can provide information about the provenance of the primary glasses (Figures 8.b and 8.c). Previous works have shown that glasses produced using sands from Egypt or Syria-Palestine present clearly different ratios between a few elements.[9] In particular, both the CaO vs SrO and ZrO_2 vs SrO ratios of the studied collection proved the existance of glasses produced from primary glasses from both regions (although Syria-Palestine glasses seem to be majoritary).



a)



b)



c)

Fig. 8. (a) Ternary diagram Na_2O-MgO+K_2O-CaO, showing the obtained experimental results by PIXE/PIGE and the classification of the main chemical groups of glass from the Bronze and Iron Ages according to the fluxing agent used: 1: Natron soda-lime glass (black), 2: Plant-ashes soda-lime glass (red), 3: Mixed soda-potash glass (blue), and 4: Forest plant-ashes, potash-lime glass. Classification between primary glasses from Egypt and Syria-Palestine regarding (b) the CaO vs SrO wt.% ratio and (c) the ZrO_2 vs SrO wt.% ratio.

Last but not least, the composition of the glass beads was stuied by multivariate analysis, which has been previously employed in the literature for the classification of ancient glasses.[10] In particular, the composition of the majoritary blue glasses was analyzed, aiming to discard obvious clustering based on the employed pigments. Moreover, only a few representative oxides were taking into account: Na_2O, MgO, Al_2O_3, SiO_2, K_2O, CaO, TiO_2, and Fe_2O_3. Figure 9.a shows the vectors of the first two principal components, PC1 and PC2, which respectively account for 29.7 and 21.3% of the variability of the analyzed data.

These two principal components allow classifying the studied blue glasses into five potential groups (Figure 9.b). Preliminary results deepening into the meaning of each of the proposed clusters provided remarkable results. For instance, when compared with the classification of the primary glasses regarding the ZrO_2 vs SrO wt.% ratio (Figure 9.c), cluster 3 clearly corresponds to primary glasses from Egypt. On the contrary, the other four clusters correspond to primary glasses from Syria-Palestine, with apparent differences regarding the SrO content, particularly for clusters 5 (lower SrO content) and 1 (higher SrO content) (Figure 9.c). It should be noted that neither the ZrO_2 nor the SrO contents were included in the multivariate analysis.

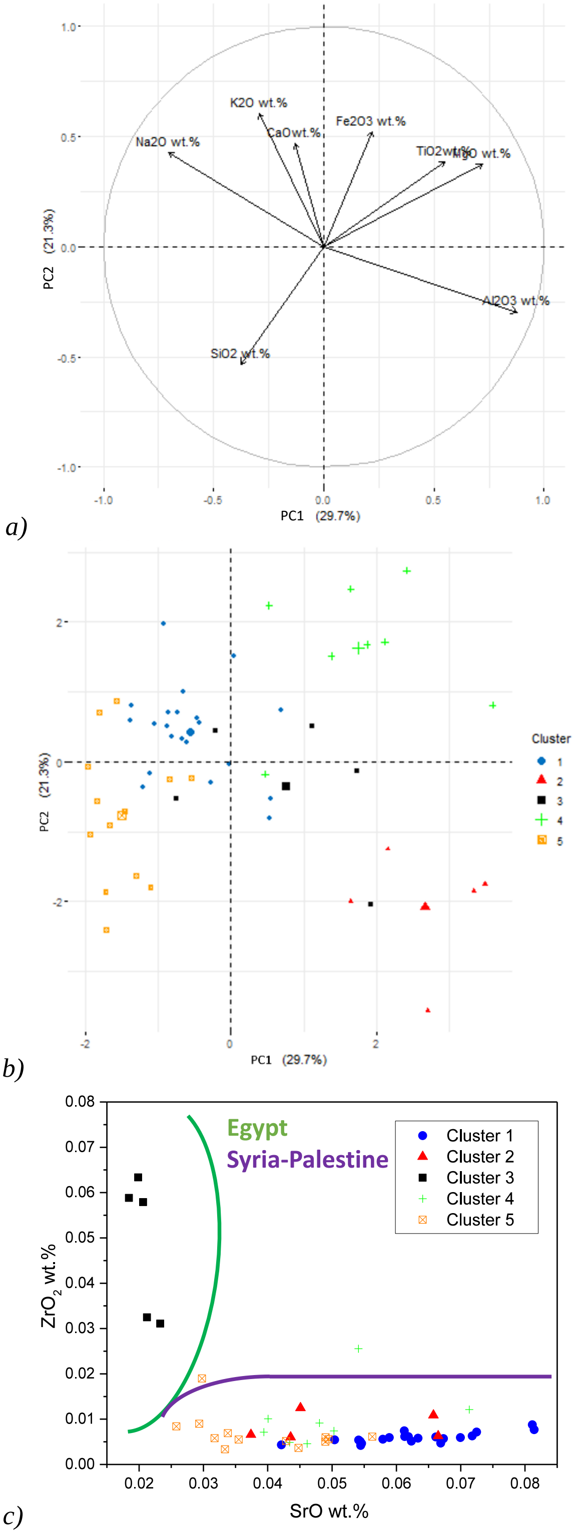


Fig. 9. (a) Vector of the first two principal components obtained by multivariate analysis. (b) PCA bi-plot of principal components 1 and 2, showing the proposed clusterization of the blue glasses. (c) Relationship between the classification between the obtained clusters and the primary glasses from Egypt and Syria-Palestine regarding the ZrO_2 vs SrO wt.% ratio.

IV. CONCLUSIONS

This non-invasive multi-technique study of a large and unique collection of pre-Roman glass beads has provided detailed and valuable information about the studied pieces. In particular, the combination of X-ray tomography, X-ray fluorescence, PIXE/PIGE, and Raman spectroscopy have allowed identifying with accuracy the diverse glass phases, their production processes (in some cases suggesting their fabrication in secondary workshops), the pigments employed to color them, the existance of diverse groups of samples regarding their manin components, and their provenance from both sands of Egypt and Syria-Palestine. The database generated in this work will serve as a reference for further studies in the Iberian Peninsula and the Mediterraneum, aiming to identify the trade routes and commertial/political relationships between pre-Roman cultures.

V. ACKNOWLEDGEMENTS

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