The Elemental Analysis of Glass Beads

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1. Introduction

Glass bead studies, using increasingly sophisticated methods, have become important in examining archaeological questions related to technology, chronology, and exchange in the ancient world. In this introductory chapter, the goal is to provide a context for the case studies presented in this volume, within the broader field of glass bead studies. For that purpose, we briefly review the history of glass bead studies: early glass bead researchers made important discoveries just by looking at the physical attributes of beads and the traces left by their manufacturing. Also, parallels made with ethnographic observations have been key to understanding the ancient technologies developed for glass bead making. We will then discuss different techniques that are applied to the investigation of glass beads, because using multiple scientific compositional and material analysis methods can provide converging evidence to validate hypotheses about manufacturing and circulation. Finally, we will present a few key discoveries related to glass beads found in regions not covered in this volume. These reinforce the importance of these small artifacts for a better understanding of ancient societies.

2. Glass bead typology and ethnography

The first bead scholars were “amateurs” with a non-academic background, only motivated by their fascination with the objects. We can consider that the study of beads started with Horace Beck (1928) and his *Classification and Nomenclature of Beads and Pendants* published almost a century ago. This important work sought to provide a precise vocabulary for the description of beads and a nomenclature for their typology. Beck, a retired designer of microscope lenses, used a microscope...
for the observation of beads, showing the path for a scientific approach to bead studies (Hutchinson 2003). All kinds of materials (glasses, stones, and metals) were considered in Beck’s 1928 volume but his geographical interest was mostly limited to artifacts from regions around the Mediterranean area and the Middle-East. The posthumous publication *A Handbook on Beads* by van der Sleen (1973) expanded bead research beyond these regions, for example, across the Indian Ocean and Western Africa. W. G. N. van der Sleen, a chemistry teacher and an adventurer, picked up a late interest in beads; he was already in his mid-sixties when he started collecting and studying them, travelling far and wide to increase his bead knowledge (Lap-Beerman 1967). Van der Sleen realized the importance of chemical analysis particularly for the “trade-wind beads” or beads circulating around the Indian Ocean in ships using the power of monsoons or trade-winds (van der Sleen 1956, 1973). Some of the chemical analysis results appear in Tornati and van der Sleen (1960) but some of the outcomes are quite puzzling (e.g., high phosphorus concentrations in Indian beads).

Several researchers followed in the footsteps of these two pioneers and refined regional bead typologies. Relevant to this present volume is the work by Kidd and Kidd (1970, 1983) who devised a classification system for European glass beads traded in the Americas. This classification, which is based on the forming techniques of the beads, their shapes, colors and decorations, was augmented by Karklins (2012) and is widely used in countries including Europe, of course, but also Africa, where relatively recent European-made beads can be found (e.g., DeCorse 1989; Hopewood 2009; Karklins and Bonneau 2019). In South Africa, Wood (2011) introduced the notion of bead series or groups of beads that share some physical attributes and that can be associated to a specific time period and sometimes, a place of origin. Wood’s system has been widely adopted in this region (e.g., Bandama et al. 2018; Tournié et al. 2012; Antonites 2014; Koleini et al. 2017). Robust glass bead classification strategies developed for specific regions and time periods are essential to place new findings in a chronological context and to accurately infer the circulation of objects between regions as further exemplified by Calmer (1977), Guido (1978) and Then-Obłuska (2021).

Peter Francis Jr. became one of the most influential bead researchers at the end of the 20th century and produced many publications about beads made of all kinds of materials and from all over the world before his premature passing in 2002. He co-founded the Society of Bead Researchers in 1981, was the editor of the Society’s newsletter *The Bead Forum*, and contributed subsequently to its journal: *BEADS* (Karklins 2002). He had a marked interest in what he called “Indo-Pacific beads,” which are part of van der Sleen’s “trade wind beads”, small monochrome drawn beads found around the Indian Ocean and beyond. Although
his many publications, including his last book *Asia’s Maritime Bead Trade: 300 BC to the Present* (Francis 2002), remain useful resources nowadays, they lack the perspective brought by the scientific analyses that started being more widely used at the end of the 1990s. His work remains, however, a solid foundation for current bead research (Carter et al. 2016).

An enduring methodological strategy that Peter Francis Jr. included in his work is the use of ethnographic observations (Francis 1991). He examined the waste produced by drawn bead production and he used this information to identify evidence of bead production at various archaeological sites across South and Southern Asia. Alok Kanungo has pursued a similar ethnographic approach in India more recently, documenting traditional glass bead making (Kanungo 2001, 2004, 2016, 2022) and providing important clues for the identification of traces of ancient glass bead workshops in the archaeological record. Literature about West African traditional bead making explores a wide range of traditional craft practices, from the production of glass to be used to make ornaments by the Nupe in Central Nigeria (Nadel and Seligman 1940; Lababidi et al., forthcoming) to the realization of powder beads in Western Africa (e.g., Agyei et al. 2012; Francis 1993; Mauny 1949).

To conclude this section, we would like to mention attempts to re-create ancient processes as a way to test hypotheses about ancient glass beads. Different sources of inspiration or guidance can be used in experimental archaeology research, such as ethnographic accounts, ancient texts or iconography, and archaeological remains (e.g., Hodgkinson and Bertram 2020; Krzyżanowska and Frankiewicz 2015). Replicating glass bead production processes helps understand not only the beads themselves, but also the archaeological signature of production waste or discards that might be identified in areas of primary and secondary manufacture.

3. The scientific analysis of glass beads

Scientific analysis provides a range of information about glass technology, chronology and exchange that is not available otherwise. As a category, it includes elemental analysis but also other types of analysis that reveal the glass recipes ancient glassmakers employed and the coloring techniques they used (Bonneau et al. 2014). Martin Heinrich Klaproth, a German chemist, is usually credited with the first elemental analysis of glass at the end of the 18th century. It is important to note that 13 g of glass were necessary for him to obtain the concentrations of a few elements by means of wet chemistry (Caley 1949). Such early methods were impractical for the study of glass beads, since most weigh less than 1 g. Presently, a range of analytical techniques with different degrees of destructiveness are
available to glass researchers. The number of elements that can be measured varies widely. Ideally, researchers choose the least destructive method able to analyze the largest range of elements with the lowest detection limits, but in practice, availability of instrumentation and the expertise of those with whom archaeologists collaborate often influence the choice of method.

X-ray fluorescence (XRF) is a well-established method for obtaining the elemental composition of glass and glass beads in particular (e.g., Dong et al. 2015; Koleini et al. 2017; Polikreti et al. 2011). This technique is quick and cost effective, although limits of detection for certain elements are fairly high and therefore only a very limited number of trace elements can be determined with this technique. It can be used in a non-destructive way on non-prepared samples, but caution is advised when objects are corroded as it only probes layers of materials close to the surface. Scanning electron microscopy (SEM) with energy dispersive spectrometry (EDS) or with wavelength dispersive spectrometry (WDS) is also an X-ray fluorescence-based technique that uses a focused electron beam instead of using an X-Ray beam to excite the sample. The interaction of the electrons with the sample creates various signals (including X-ray fluorescence) providing information about the surface topography of the glass and its composition. The imaging capability of the SEM makes it possible to look at the composition of inclusions and other heterogeneities in the glass or to map the distribution of elements over the surface of the sample (e.g., Li et al. 2013; Shortland et al. 2018). SEM-WDS and electron probe micro-analyzers or EPMA are fairly similar technologies, but EPMA is able to detect a larger range of elements and with lower detection limits compared to SEM. It can probe tiny surfaces with a diameter smaller than 1 micron (e.g., Purowski et al. 2012). Best results (for EPMA and SEM) are obtained on flat and polished samples usually coated with a conductive material such as carbon.

Neutron activation analysis (NAA) is a bulk technique able to quantify a large range of elements with a sensitivity that can reach the ppb level. It can be totally non-destructive. It has been used quite extensively for the study of ancient glass beads as exemplified by the work of Hancock in North America (Hancock 2013; Hancock et al. 1994, 2000), Davison in Africa (Davison 1972) and Rahman in Southeast Asia (Rahman et al. 2008).

Another bulk analytical technique used with ancient glass beads is atomic emission spectrometry (AES) also called optical emission spectrometry (OES), which can determine the concentrations of up to 70 elements including traces but requires that a small quantity of the bead (or the whole bead when very small) is dissolved into a solution (e.g., Zhang et al. 2005).

Today, an increasingly popular technique for the analysis of glasses and glass beads in particular, is laser ablation - inductively coupled plasma - mass
spectrometry (LA-ICP-MS) because it can analyze the smallest beads (~ 1mm in diameter) without visible damage. The laser can individually pinpoint the different colors of a polychrome bead. It is fast, so 40-50 beads can be analyzed in one day, and it is relatively affordable. Additionally, LA-ICP-MS can determine the concentrations of a very large range of elements (up to 60-65). For these reasons, the contributing authors of this volume have relied on LA-ICP-MS to analyze beads from sites that they are researching around the world. This work is especially valuable because the LA-ICP-MS dataset presented here has been obtained exclusively at the Elemental Analysis Facility (EAF) of the Field Museum, using the same approaches to quantification and data analysis, making the compositions highly comparable both to one another and to other published datasets generated there. In Annex A, Dussubieux provides a comprehensive overview of how these methodologies have been applied consistently under her supervision at the EAF, which has operated LA-ICP-MS for archaeological analyses since 2005. In Annex B, we summarize findings of previous scientific analyses of glass beads, which have identified temporally and geographically relevant compositional groups.

In combination with elemental analysis methods, additional tools are available to help define the structures of glasses and in some cases assist in identifying the ingredients or raw materials used in the production process. For example, X-ray diffraction (XRD) is able to identify the crystalline phase present in the glass, which is useful because it can help identify whether a particular mineral was brought by the raw materials or produced during the manufacturing process, generally to color and/or opacify the glass. XRD can be applied to a whole object in a non-destructive manner but better results are obtained on powdered samples (Zhu et al. 2012).

Raman spectroscopy is increasingly used to study glass and glass beads in particular because this technique can help identify the type of glass and provide insight into the coloring technology (e.g., Costa et al. 2019; Pinto et al. 2021; Prinsloo and Colomban 2008). This technique has the great advantage of being totally non-destructive and portable instruments facilitate the study of in-situ materials, artifacts that are difficult to move to scientific laboratories, or large objects that do not fit the fixed geometry of some benchtop instruments (Colomban et al. 2021; Sánchez et al. 2019). Raman is measuring radiations that are scattered by a material illuminated by a light beam (usually a laser). A small proportion of an incident beam directed at the surface of a glass object will be scattered in all directions. Although most of the scattered radiation will keep the same wavelength as the incident radiation, a very small quantity will have a different wavelength. This wavelength difference will be characteristic of the material (Pollard et al. 2007: 83).
The question of the provenance of the raw glass used to manufacture glass objects and more specifically beads is often difficult to elucidate because the absence of archaeological evidence (in the form of manufacturing tools, production waste, or unfinished objects) often prevents the identification of potential primary glass workshops. Isotope analysis can help connect the raw ingredient material to the region it was extracted from. It relies on the fact that the isotope ratios of certain elements entering the composition of glass remain unchanged through the manufacturing process and are identical, within analytical error range, in the initial raw material and in the final product (Brill and Wampler 1967). Isotope analysis in glass started with the measurement of lead isotope ratios by Robert Brill, who tried to link the lead in glass with a possible source region where it could have been procured (Brill 1969). Lead is often used (in combination with other elements) as an opacifier, as a flux (in place of or in combination with an alkali-rich ingredient), or as a primary glass-former (in later glasses), and thus is often present in minor to major concentrations in glass. Despite promising results, provenancing a colorant or an additive is not always ideal, as they can be imported and have a significantly different provenance compared to the glass itself (Barnes et al. 1986; Brill 1969; Brill et al. 1973, 1974; Shortland 2006). By contrast, silica, which is the primary constituent in glass, is generally assumed to come from a source such as sand from near the glass production site. This is because of its intrinsic low value, the large quantities of silica required to produce glass, and the expense of moving this ingredient over long distances; therefore, it can be inferred to be geochemically linked to the producing population/culture. Actually, the location of a primary glass workshop was quite likely chosen according to the proximity of a suitable silica source and the availability of fuel, also bulky but whose value depends on environmental availability. More recently, strontium (Wedepohl and Baumann 2000; Freestone et al. 2003) and neodymium (Degryse and Schneider 2008) isotopic systems have been used for provenancing lime and silica sources, respectively. Strontium is incorporated into glass with lime-bearing constituents and was found to be derived from beach shell and/or limestone in natron glass and from plant ash in glass made from halophytic (salt-tolerant) plants (Degryse et al. 2009). Neodymium originates from the heavy or non-quartz mineral component of the sand/silica used (Degryse et al. 2009). This approach has been used recently for a large-scale project conducted by Degryse and his colleagues aimed at identifying the primary provenance of natron glass from the Roman period in the Mediterranean (Degryse 2014) and for beads from different regions (e.g., Dussubieux et al. 2021; Van Ham-Meert et al. 2019). The development of new sampling tools that avoid the full destruction of small beads will certainly motivate even more research with this kind of approach (Seman et al. 2021).
4. A few notable discoveries related to glass beads

The array of methods and advances in archaeological sciences in recent decades has led to a florescence of research on glass beads worldwide. Although this volume only includes two major geographic areas of emphasis: Indian Ocean exchange networks and beads produced in Europe for trade to the Americas (and other regions of colonial interest) in the 16th to 19th centuries, we would like to highlight several other areas of bead studies. Although this section is by no means an exhaustive summary about glass bead research in general, these findings are extremely important to understanding the production, circulation, and meanings of glass beads in a more comprehensive fashion.

While the earliest origins of glass making are still ambiguous, archaeological evidence clearly shows that around the middle of the 2nd millennium BCE, prosperous glass industries were thriving concomitantly in Egypt and Mesopotamia (Shortland et al. 2018). Objects manufactured at this early period included beads. The trace elements signatures of glass artifacts found in both regions as determined by LA-ICP-MS have been key to differentiating the two industries and tracking them around the Mediterranean basin and beyond (Purowski et al. 2018; Shortland et al. 2007; Smirniou et al. 2012; Varberg et al. 2015; Walton et al. 2009). For example, the discoveries of Egyptian and Mesopotamian glass in Denmark have revealed contact between these regions dating from the fourteenth to twelfth centuries BCE. Although finished objects were traded, raw glass was also procured by beadmakers who would transform it into objects reflecting local tastes, as attested by the discovery of beads with a Mycenaean style manufactured with glass from Egypt and Mesopotamia (Smirniou et al. 2012; Walton et al. 2009) and the recovery of ingots on their way to secondary glass workshops, from the Late Bronze Age Uluburun shipwreck (Jackson and Nicholson 2010).

Subsequent cultures around the Mediterranean and across Europe continued to produce and exchange glasses for the production of beads and ornaments as well as other finished forms. The glass beads produced by Hellenistic and Celtic cultures in this region are a topic of current studies with LA-ICP-MS and other methods, shedding light on primary production centers and secondary workshop organization across Europe in both the early Iron Age Hallstatt (roughly the eighth to sixth century BCE) and the later La Tène (fifth to first century BCE) periods. The site of Sardis, in present-day Turkey, has recently been identified as a glass bead production site as early as during the eighth century BCE (Van Ham-Meert et al. 2019). Some glass beads found in present-day Poland at Hallstatt C-D sites are apparent imports to that region (Purowski et al. 2012; 2020). Later, La Tène imports of raw glass from Egypt and the Levant have been identified in
central Moravia, for example (Rolland and Venclová 2021; Venclová 2016). A comprehensive summary of the extensive ongoing research on Iron Age European glass production and exchange is beyond the scope of this introductory chapter, but it suffices to say it rivals the current flurry of studies about Indian Ocean exchange networks.

While around the same period (as early as the 5th century BCE) some of the glass production of the Levant was traded westward around the Mediterranean area and with Europe, glass beads from the same region were also exchanged eastward along what was called the “Proto-Silk Road” and have been found in China (Lü et al. 2021). There, it seems that the availability of this new vitreous material stimulated technological innovation leading to the first lead-barium glass obtained by mixing imported glass from the Mediterranean region and local lead and/or barium-containing minerals (Ma et al. 2022). The Silk Road was a very important route for the circulation of glass (and glass technology) between the Mediterranean world and China but its influence was not limited to its end points as glass can be detected all along its path (Fuxi et al. 2009).

Several chapters of this volume deal with glass beads found in Sub-Saharan Africa, but they are all concentrated in the eastern part of the continent. There, glass beads were mostly imported goods. In western Africa, recent discoveries of an indigenous glass bead making industry in the Ile-Ife region of Nigeria have revealed the development of a local glass recipe taking advantage of the availability of a pegmatite sand with high alumina concentrations that was mixed with high lime snail shells. This created a high lime - high alumina (HLHA) glass used to produce beads that were traded all over western Africa during the first half of the 2nd millennium CE (Babalola et al. 2018a, 2018b; McIntosh et al. 2017; Ogundiran and Ige 2015; Lankton et al. 2006). A lot of questions remain about the glass beads from Ile-Ife. What motivated this innovative way to manufacture glass? Why did it happen in this part of Sub-Saharan Africa and not elsewhere? As archaeological sites in the Global South continue to receive more scholarly attention, these are examples of questions that could be addressed with further LA-ICP-MS studies.

5. Conclusion

This chapter has shown how in the past decades (and almost century) we have seen major advancements in the way glass beads are studied. Yet, the importance of these small artifacts has often been neglected in favor of scholarship on glass vessels, ceramics, or metal objects, for example. Due to their small size, beads certainly have a more limited number of typological or functional attributes than
other larger artifacts, limiting the depth of the archaeological interpretation. With the increased use of analytical techniques, additional information can be extracted from ancient glass beads, making them more meaningful artifacts. With the more general use of these techniques and LA-ICP-MS more specifically, as evidenced by the different projects presented in this volume, glass bead research has jumped forward significantly in recent years as a dedicated archaeological specialization.

References


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