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Analysis of early medieval glass beads – Glass in the transition period

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ABSTRACT

Glass beads from graves excavated in Slovenia and dated archaeologically to the 7th–10th century AD were analysed by the combined PIXE–PIGE method. The results indicate two groups of glass; natron glass made in the Roman tradition and glass made with alkalis from the ash of halophytic plants, which gradually replaced natron glass after *c.* 800 AD. The alkalis used in the second group of glass seem to be in close relation to a variant of the Venetian white glass that appeared several centuries later. The origin of this glass may be traced to glass production in Mesopotamia and around the Aral Sea. All the mosaic beads with eye decoration, as well as most of the drawn-segmented and drawn-cut beads analysed, are of plant-ash glass, which confirms their supposed oriental origin.

1. Introduction

Roman and post-Roman glassmaking was specialised and regionalised, allocating production of raw glass to the geographical area of Egypt and Palestine [1]. Raw glass was produced in huge blocks, exploiting local siliceous sand from the coast, naturally enriched by calcium from sea shells, and the alkali sediments from Egyptian wadis; this is known today as natron [2]. These two components provided all the necessary ingredients of glass: a siliceous matrix (with Ca as stabiliser) and a relatively pure alkali flux. Chunks of raw glass were then distributed, mainly through sea trade, to the secondary workshops where they were reworked into final products. Local treatment also included decolouration and pigmentation. The influence of impurities, which mainly originated from the sand component, was neutralised by decolourisers, typically manganese and antimony oxides [3].

The present state of research suggests that political events in Egypt, starting with the Persian invasion in 619, continuing with a complex Muslim–Christian conflict in the 7th and 8th centuries, and the Berber invasion in the 9th century, strongly disturbed access to natron sources [4]. As a response, a new technology of obtaining alkalis was developed in the Byzantine or/and Islamic world. Alkalis with a large fraction of sodium were obtained from the ash of halophytic plants. In the past, plant ash had already been used in Bronze Age Egyptian and Mesopotamian glassmaking [5].

The transition to the new alkali source was not immediate, especially as large quantities of natron-type glass were circulating in the former Roman world [6]. Natron-type glass was identified in Late Roman/Early Christian centres, like San Martino di Ovaro in Northern Italy [7], Jarrow in England [2] and Tonovcov grad in Slovenia [8]. The glass beads in circulation in the Merovingian kingdom (middle of the 5th – middle of the 8th century) were also of the natron-type [9,10]. Natron-type glass is also known from 6th to 7th century Byzantine sites in the Eastern Mediterranean [11–13], Sicily [14] and Padua [15]. Glass of both natron and plant-ash type was found in the 8th–10th century site of Carvico in Northern Italy [16] and in a broad area of the Venetian lagoon (glass samples dating between the 7th and 13th century) [17]. The introduction of halophytic plant-ash that started at the end of the 8th/beginning of the 9th century was probably completed in the 13th century [18], which coincides with the development of Venice into a strong glass production centre.

Sites containing both natron and halophytic plant-ash glass are at present rare. Analysis of glass from the 6th and the end of the 8th to the beginning of the 10th century site of Gradišče above Bašelj in Slovenia showed it was all natron-type, except for two glass beads that were made of glass produced from the ash of halophytic plants [19]. Glass beads very likely spread faster than any other glass items. A few examples of plant-ash glass beads were also encountered among the early medieval beads from Strömkendorf in northern Germany [20].

Glass beads are an important time indicator, and therefore we designed an investigation of 97 glass beads found in cemeteries from the 7th to beginning of the 11th century in Slovenia (Fig. 1). They included six mosaic beads with eye decoration

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Fig. 1. Earrings with beads, necklaces and mosaic beads with eye decoration included in the study. Sites: Brda near Bled (1,3:), Pristava near Bled, graves 65, 141, 192 (2, 4, 5), Bela Cerkev near Šmarjeta (6), Pržan near Ljubljana (7, 8).

(*millefiori*, *Mosaikaugenperlen*) and several drawn-segmented and drawn-cut beads that often occur in graves together with mosaic beads. In archaeological publications, several types of such beads are regarded as being of oriental origin and are dated to the end of the 8th, and especially to the first half of the 9th century [21–24].

The beads included in the analysis came from sites that on archaeological grounds belong to two cultural groups. The first group, dated to the end of the 8th and to the 9th century, is represented by cemeteries in eastern Slovenia, for which pottery grave goods are characteristic [25]. The second group is the Köttlach culture in central Slovenia. Central European scholars date its beginning, i.e. its earliest stage (*Vor-Köttlach-Horizont*) to the first half of the 9th century and its later stages (*Köttlach I and II*) from the second half of the 9th to the first half of the 11th century [26]. In contrast, Slovenian archaeologists date its beginning (which they describe as the Caranthanian cultural group) earlier, i.e. to the 7th and 8th century, and its later stages (Köttlach cultural group in the narrow sense) to the 9th and 10th century [27].

2. Experimental

Analysis was performed at the Tandetron accelerator of the Jožef Stefan Institute in Ljubljana, using a proton beam in air. The method of proton-induced X-ray emission (PIXE) was used for analysis of elements heavier than silicon. The nominal proton energy was 3 MeV, which was reduced to approximately 2.7 MeV at the target, after passing an 8 μm Al window and a 1 cm air gap. A Si(Li) X-ray detector of 160 eV resolution at 5.89 keV was positioned at 45° with respect to the target normal. The air gap between the detector and target was 5.7 cm. The experimental geometry was maintained by nylon spacers; these replaced the previously used metal spacers made from nickel-plated needles, as the scattered protons also excited nickel atoms in the needles, thus worsening the detection limit for nickel to about 0.1%. Precise values of the air gaps were determined by measurements of a series of single-element and simple chemical compound targets, exploiting the signal from air argon for normalisation.

Two sequential measurements at the same spot were performed, one using the air gap as the only absorber, and the other using an additional absorber of 0.1 mm Al foil. The beam profile was approximately Gaussian, with 0.8 mm full width at half maximum (FWHM) at the target. The proton current was a few tenths of a nA for the first measurement and about 1 nA for the other, and the measuring time was 300–500 s. In this way we increased the sensitivity for mid-Z elements around Sr to about 10 μg/g. Spectral de-convolution was performed by the AXIL program and the two sets of X-ray intensities were combined into one using the Fe Kα line for normalisation.

As silicon was the lightest element detected, the concentrations of the essential glass elements Na, Mg and Al were determined from the yields of excited gamma rays (PIGE). A 2 μm thick Ta foil was used for the exit window, in order to reduce the background gamma radiation to sub-100 keV energies. The Ta foil was not used for X-ray measurements, as its M and L X-rays, which reached the detector on account of scattering in the air, would coincide with the X-rays of silicon and copper, respectively, from the target. The number of incident protons was measured by a thin wire mesh intersecting the beam before the exit foil. The transmission of the mesh was about 58% [28]. This type of measurement appeared more efficient than monitoring of silicon gamma lines, as their intensities decrease rapidly at proton energies below 3.1 MeV [29]. For example, at 2.4 MeV, production of the 1779 keV line in silicon is 36-times weaker than in aluminium [30].

The induced gamma rays were detected by a 40% efficiency intrinsic Ge detector. Gamma lines, produced by inelastic proton scattering, were observed at 440 keV for Na, 585 keV for Mg, and 844 and 1014 keV for Al. The latter two lines are also produced by a (p, γ) reaction in magnesium, though its contribution at energies above 1.7 MeV is negligible [30]. We also measured the count rate of the natural gamma line at 583 keV that coincides with the Mg line. As a result of the lead shielding of the detector and a sufficient count-rate of the proton-induced gamma rays, its intensity was below 10% of the Mg line induced in plant-ash glass, but of comparable intensity in the natron-type glass. The detection limit for MgO was thus estimated to be about 0.3%. For PIGE measurements, the proton current used was ~3 nA and the accumulated dose was 3 μC. A higher dose of 12 μC was used for the NIST 620 glass standard, which served for calibration. The gamma ray intensities were determined by the GRILS program of the GANAAS package.

The evaluation of elemental concentrations was made by an iterative procedure, considering the induced X-ray and gamma ray intensities simultaneously. The concentrations of Na, Mg and Al were calculated by the surface approximation [31], except that the necessary stopping power data were included iteratively, in the same way as the matrix effects for the induced X-rays. The elements were assumed to be in oxide form, and the sum of oxides was normalised to unity. As the shape of the beads departed considerably from the plane geometry assumed in the evaluation program, the following procedure was applied: The contents of Na_2O, MgO and Al_2O_3 obtained by PIGE were not re-normalised, as the more penetrative gamma rays did not attenuate in the target. The measured proton doses were further regarded as reliable, since any mishit of the proton beam for small beads was monitored by a scintillator positioned behind the target. From the total content of Na, Mg and Al oxides the code calculated the fraction of remaining metal oxides and normalised the concentrations obtained from the X-ray intensities to this value. However, the actual oxide sum could also be monitored with respect to the intensity of the Ar line in air, which measured the proton number for PIXE measurements. The distribution of these values is quite broad (Fig. 2), though it peaked at 0.9, i.e. close to unity.

By simulation, using a variable set of input parameters in the calculation, we found that the reason for this distribution is geometrical. As a test we chose a measurement with the sum of non-normalised oxide concentrations of 0.6, roughly exceeding the range of the left peak in Fig. 1. A unit sum was obtained by increasing the air gaps travelled by protons and X-rays by 2.1